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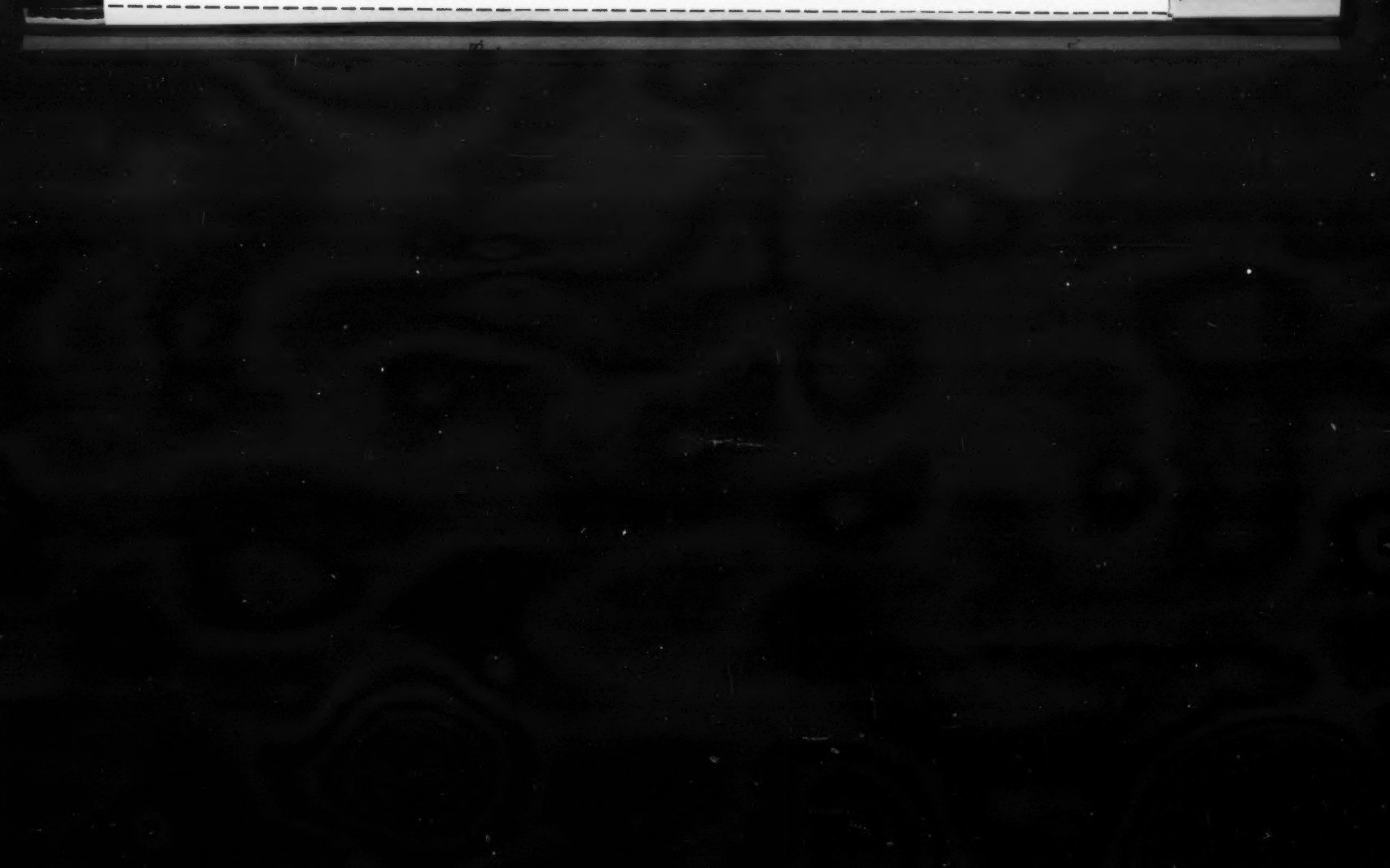

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QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*Contributions to the knowledge of the Laws of Gas-absorption.*

By Thos. H. Sims,

(Dalton Scholar in the Laboratory of Owen's College, Manchester).

It is well known that some gases, which at a given temperature obey, between certain limits, Boyle's law of pressure, have been found to deviate from the law when examined between the same limits of pressure, but at different temperatures. Thus Regnault* has shown that the volumes of carbonic acid gas measured, under different pressures less than that of the atmosphere, at the temperature of 0° C, do not vary inversely with the pressure; whereas measured between the same limits of pressure at 100° C., the deviation from Boyle's law becomes inappreciable. Considering these facts, it appeared not unlikely that the law known as Dalton and Henry's Law, according to which the weight of gas absorbed by a liquid at a given temperature under various pressures, is directly proportional to the pressure, would, upon investigation, show phenomena of a similar kind, so that the amount of deviation from the law of absorption which a given gas exhibits between certain limits of pressure may vary according to the temperature at which the absorption occurs. That many of the gases most soluble in water are not absorbed at the ordinary temperatures under different pressures in proportions even approaching those required by Dalton's law, has already been pointed out. Professor Roscoe† showed that chlorine gas,

* Regnault, Expériences pour déterminer, &c., p. 148.

† Chem. Soc. Qu. J., viii. 14.

when mixed with varying amounts of both hydrogen and carbonic acid gas, is not absorbed in quantities proportional to the pressure; and Messrs. Roscoe and Dittmar* have recently proved that under directly measured pressures extending from 0·05 to 2 metres of mercury, both hydrochloric acid and ammoniacal gases are absorbed by water at 0° C., in quantities differing widely from those required by Dalton and Henry's law.

Experiment has, up to the present time, left it undecided, whether this deviation from the law of absorption is solely dependent upon the chemical nature of the gases and liquids present, or, whether the relation between the amount of absorbed gas and pressure is at the same time influenced by change of temperature.

The object of the present research is to throw some light upon this question by determining the solubility of certain gases in water under considerable variation of direct pressure at different temperatures.

1.—*Sulphurous Acid in Water.*

The solubility of sulphurous acid gas in water, at various temperatures, and under the ordinary atmospheric pressure, has already been accurately determined by Schönfeld,† but no estimation of the quantity of gas absorbed under directly increased or diminished pressures has been made. Hence it appeared desirable to examine whether the conclusion drawn by Schönfeld from experiments made with mixed gases, viz., that at temperatures above 10° C., sulphurous acid obeys the law of absorption, was borne out by more extended observations of the solubility of the gas under directly measured pressures. For this purpose, a method of experimentation was adopted, similar in principle to that described by Messrs. Roscoe and Dittmar, in the memoir already mentioned, viz., determining by accurate analysis the quantity of gas absorbed by a known weight of water contained in a bulb-tube apparatus, under exactly specified conditions of temperature and pressure. The amount of the dissolved gas was estimated, according to the iodometric method, by carefully breaking the bulb under recently boiled water, diluting the solution to a given volume, and analysing an aliquot portion of the liquid again diluted with water, so that it contained only 0·05 p. c. of sulphurous acid. The strength of the standard iodine-solution was not determined

* Chem. Soc. Qu. Jn., xii., 128. † Ann. Ch. Pharm., xcv., 1.

in the usual way, by comparison with the iodine equivalent to the chlorine set free by hydrochloric acid, from a known weight of bichromate of potassium, but the volume of the standard solution was directly determined, which was required to oxidise completely a given weight of pure dry sulphurous acid, diluted with water to such an extent that the liquid contained only 0·05 p. c. of sulphurous acid. For this purpose, long-necked tubes, represented by Fig. 1, were blown before the blowpipe and accurately weighed; into these tubes was led a quantity of pure and dry sulphurous acid, which had previously been distilled and left no residue on evaporation. As soon as from 1 to 2 grms. of the liquid had collected in the tubes, they were hermetically sealed, and again weighed. When the determination was to be made, the neck of one of these tubes was opened under recently boiled water, whilst the bulb was placed in a freezing mixture, which was afterwards removed, so that the liquid acid began to distil over into the water. As soon as the acid had volatilised, and the water had been drawn back into the tube, the neck was cut off with a file, and both tubes washed well out with water. The solution of sulphurous acid was then diluted with boiled water up to 3,600 cb. c.; of this diluted solution, 100 cb. c. were taken for analysis, and the standard iodine solution was added drop by drop from a burette until the blue starch reaction became visible. From the quantity of solution thus required, and from the quantity of sulphurous acid employed, it was easy to find the weight of sulphurous acid corresponding to one cubic centimetre of iodine-solution. The following numbers give the weights of sulphurous acid oxidised by 1 cb. c. of the standard solution, as determined for solution No. I by four, and for solution No. II by six, separate experiments:

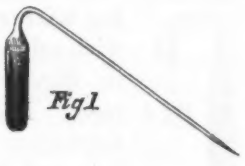


Fig 1

Solution No. I.		Solution No. II.	
Experiment 1 ..	0·001212	Experiment 1 ..	0·001200
„ 2 ..	0·001211	„ 2 ..	0·001208
„ 3 ..	0·001216	„ 3 ..	0·001204
„ 4 ..	0·001211	„ 4 ..	0·001210
		„ 5 ..	0·001200
		„ 6 ..	0·001210
Mean	0·001212	Mean	0·001205

In order to avoid the dangerous explosions which might ensue from the employment of flasks in which the gas is prepared from heated sulphuric acid and copper under a pressure of from two to three atmospheres, the liquefied acid was used as the source of gas. The supply of gas was obtained in a convenient form by evolving it in the usual manner from sulphuric acid and copper, and by well washing it through bulbs containing water, then passing it into glass tubes with long necks of about 15 cb-cs. capacity placed in a freezing mixture. As soon as the tubes were nearly filled with sulphurous acid, the necks were bent, as shown in Fig. 2, and afterwards closed before the blow-pipe. Each tube contained a sufficient quantity of sulphurous acid for one experiment, the tube *b* being of the same diameter as the neck of the bulb-apparatus to which it was directly attached.

Fig 2

Different arrangements of the same method were adopted, according as the determination was to be made under a pressure, equal to, greater, or less than, the ordinary atmospheric pressure. For determining the absorption under ordinary pressures, one of the tubes of sulphurous acid was placed in a freezing mixture and opened by cutting off the narrow tube at *b*, Fig. 2, the end of this tube was then rounded before the blow-pipe, and connected by a carefully made double-sheet caoutchouc joining with the end *a* of a bulb apparatus, Fig. 3, of which the capacity and weight were known. The bulb *e* of this apparatus, capable of containing from 2 to 5 cb-cs. water, was placed in a water-bath, which was provided with arrangements for the supply of hot and cold, and for the egress of waste water. In this water-bath, and near to the bulb apparatus, was placed a thermometer which had been carefully compared with a normal instrument from the Kew Observatory. The temperature of the bath was easily kept constant at any required point, by continual agitation with a stirrer, and by running in, as required, hot or cold water. The apparatus was so arranged that the tube of liquid acid was fixed outside the water-bath, and at such a distance from it, that when operating at high temperatures, the heat might not cause too rapid an evolution of gas. In this way, a very steady stream of sulphurous acid could be passed through the bulb-tube without the slightest difficulty; the ordinary temperature of the atmosphere

Fig 3

not being high enough to cause the gas to be given off too quickly, and the evaporation from the surface of the liquid acid cooling it down considerably. After the liquid in the bulb had been saturated, the gas was still allowed to pass through it for about 20 minutes longer in order to insure that the liquid attained the exact temperature of the water-bath. The limb of the bulb nearest to the tube of sulphurous acid was then closed by pressing the caoutchouc joining with a screw-clamp, and afterwards the other limb by pressing in a similar way a sheet-caoutchouc tube with which it was provided. The bulb was then separated from the tube of sulphurous acid, removed from the water-bath, placed in a freezing mixture and hermetically sealed at *c* and *d* (Fig. 3). The height of the barometer was then observed; the bulb and its contents, together with the ends of each limb, were again weighed; the temperature in the balance-case was noted; and also the height of the barometer at the time of weighing. The bulb was next carefully broken under water, and the solution diluted with water up to a certain known volume, such that the liquid did not contain more than 0·05 p.c. of sulphurous acid, the water in both cases having been recently boiled. An aliquot portion of this was then taken for analysis, and the amount of sulphurous acid it contained, was determined by the addition of starch and a standard iodine-solution, of which every cubic centimetre corresponded to a certain known weight of sulphurous acid.

From these data, the weight of sulphurous acid absorbed by one gramme of water at the observed pressure and temperature was easily calculated. An example will best show the mode of calculation. The following were the data obtained in one experiment :

Weight of bulb-apparatus empty	=	21·0399 grms.
Capacity of apparatus to *c d*.	=	18·38 cb.c.
Weight of bulb and contents	=	24·3800 grms.
Barometer at closing	=	746·9 mm.
Temperature of bath	=	20° C.
Barometer at weighing bulb and contents	=	748·2 mm.
Temperature in balance-case at weighing bulb and contents	=	14° 5 C.
Tension of aqueous vapour at 20° C.	=	17·4 mm.

The contents of the bulb diluted up to 1000 cb. c., of which 100 cb. c. required for oxidation 28·1 cb.c. of a standard iodine-

solution, of which 1 cubic centimetre corresponded to 0·001212 grm. of sulphurous acid.

1000 cb. c. of sulphurous acid at 0° C. and 760 mms. weigh 2·8606 grms.

1000 cb. c. of air at 0° C. and 760 mm. weigh 1·294 grms.

From the above data we find that the total quantity of sulphurous acid would require 281 cb. c. of iodine solution. The whole of the sulphurous acid contained in the bulb weighed, therefore, $281 \times 0{\cdot}001212 = 0{\cdot}3406$ grm. The capacity of the bulb at 0° C. and 760 mms. was found to be 17·03 cb. c. The weight of this volume of air is 0·022 grm. The contents of the bulb, viz., the water and total sulphurous acid weighed $24{\cdot}38 - 21{\cdot}0399 = 3{\cdot}3401$ grms. The weight of the contents and the weight of air displaced may therefore be taken as $3{\cdot}3401 + 0{\cdot}022 = 3{\cdot}3621$ grms. This being taken as the capacity of the liquid in cubic centimetres, the volume of sulphurous acid gas contained in the bulb at 20° C., and under a pressure of $746{\cdot}9 - 17{\cdot}4 = 729{\cdot}5$ mm. is $18{\cdot}22 - 3{\cdot}36 = 14{\cdot}86$ cb. c. The weight of this gas was found to be 0·0382 grm. The sulphurous acid dissolved is, therefore, $0{\cdot}3406 - 0{\cdot}0382 = 0{\cdot}3024$ grm. The weight of water which dissolves this weight of sulphurous acid is therefore $3{\cdot}3621 - 0{\cdot}3406 = 3{\cdot}0215$ grms.

The weight of sulphurous acid which 1 grm. of water will dissolve at a temperature of 20° C. and a pressure of 729·5 mm. is therefore, $\frac{0{\cdot}3024}{3{\cdot}0215} = 0{\cdot}1002$ grm. The volume of sulphurous acid measured at 0° C and 760 mms. which 1 grm. of water will dissolve, under the same circumstances, is found to be $\frac{105{\cdot}7}{3{\cdot}0215} = 35{\cdot}0$ cb. c.

If the amount of gas absorbed were directly proportional to the pressure, at a temperature of 20° C., and under the normal pressure of 760 mm., 1 grm. of water would dissolve 0·1043 grm. and 1 cb. c. would dissolve 36·47 cb. c. of sulphurous acid.

Under pressures greater than that of the atmosphere, a bulb-apparatus similar to that used for ordinary pressures was employed. The requisite quantity of boiled water having been introduced into the bulb, a tube of liquid sulphurous acid *f* was attached by means of a sheet-caoutchouc joining to the limb *a* of the bulb (Fig. 4); to the other limb *b* was attached in a similar way, the burette-shaped apparatus C., which, filled with mercury, is used for obtaining the necessary pressure. Between the tubes, thus connected with

caoutchouc joinings, sufficient room was left, to allow them to be closed with screw-clamps at the conclusion of the experiment. To render these joinings able to withstand the pressure, they were first bound tightly to the respective tubes with copper wire, and over the middle portion of each of those joinings, a piece of brass foil was tightly folded which was allowed to overlap the glass tubes at both ends. Each of the ends of these pieces of foil was then tightly bound round with strips of sheet-lead, and these were secured to the tubes, by means of small iron semicircular screw-clamps (Fig. 4 *g*).

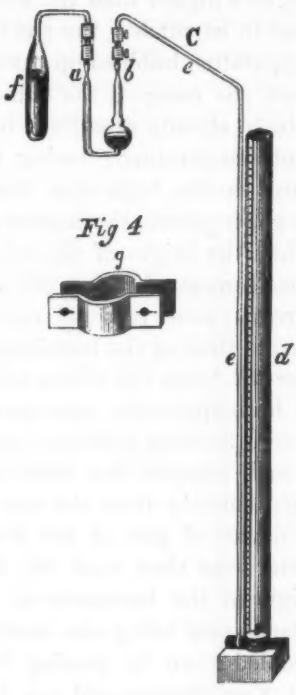


Fig 4

The apparatus thus put together was perfectly air-tight under pressures up to three atmospheres, and could be closed at pleasure, by pressing together the copper foil with screw-clamps. Into the wide tube *d* of the apparatus C, which was divided into millimetres, and was about 2000 mm. long, a small quantity of mercury was placed, so as to shut off all access of air to the other part of the apparatus. When the sulphurous acid evolved from the liquid acid in the tube *f*, and passing through the water in the bulb-apparatus, had expelled all the air from the apparatus, mercury was by degrees poured into the divided tube *d*, until the necessary pressure was reached; the joining nearest the tube of sulphurous acid was then closed, by means of a screw-clamp; the bulb-apparatus was placed in a freezing-mixture; and when the rise of the mercury in the tube *e* of the apparatus C, above that in the tube *d*, indicated a minus pressure in the bulb-apparatus, the sulphurous-acid tube was removed by sealing off the bulb-apparatus at the narrowed part of the limb *a*. The temperature of the freezing mixture was then gradually increased by pouring in water, until it became one or

two degrees higher than the temperature at which the determination was to be made; the gas thus set free from the water in the bulb-apparatus, bubbled up through the mercury in tube *d*. When no more gas escaped, the bulb-apparatus was transferred to the water-bath, already described, in which it was kept at the required constant temperature; owing to the reduction of temperature the water in the bulb now dissolved a further quantity of gas, and in consequence, the mercury rose a small distance up the tube *e*. When the height of the column of mercury in this tube had remained constant for 20 or 30 minutes, the heights of both columns of mercury were read off on the scale upon the wider tube *d*. The second limb of the bulb-apparatus was then closed by pressing together the brass foil with a screw-clamp.

The bulb-apparatus was next removed from the water-bath, placed in a freezing mixture, and as soon as the tension of the liquid had become less than the pressure of the atmosphere, separated entirely from the rest of the apparatus by sealing it off at the narrowed part of the limb *b* (Fig. 4). The height of the barometer was then read off, the bulb and its contents weighed, the height of the barometer at weighing and the temperature of the balance-case being also noted. The contents of the bulb were then cooled down by placing it in a freezing mixture, and the amount of sulphurous acid was determined, as before described, by breaking it under recently boiled water, diluting the solution to a certain known volume, and taking an aliquot portion of this solution for iodometric analysis.

In order to determine the amount of the gas dissolved under pressures less than one atmosphere, the method was modified in the following manner. Instead of the bulb-apparatus (Fig. 3) employed in both the former cases, a simple bulb (Fig. 5) blown upon the end of a glass tube was made use of. These bulbs had a capacity of, from 10 to 30 cb.cs. Into one of such bulbs was introduced from 5 to 15 grms. of recently boiled water, which was then saturated with sulphurous acid, evolved from one of the tubes of liquid acid the water being kept just above 5° C., at which temperature the solid hydrate melts. As soon as the water in the bulb was saturated with sulphurous acid at this temperature, a sheet-caoutchouc tube containing a spiral of platinum wire, was bound with copper wire, on to the open end of the

Fig 5

bulb-tube. This bulb-tube was then connected in a similar way, by the other end of the caoutchouc tube, to the shorter limb of a syphon-shaped tube (Fig. 6), the longer limb of which was divided into millimetres and dipped under mercury contained in a glass trough. The syphon-shaped tube was previously filled with sulphurous acid gas.

Fig 6

When the apparatus was thus arrranged, the liquid in the bulb was gradually heated; large quantities of sulphurous acid were thus evolved, and consequently the apparatus was soon freed from air. According as it was desired to have a greater or a less pressure, a smaller or larger amount of gas was expelled. The requisite amount of gas having been driven out, the bulb was placed in the water-bath, and kept constantly at the required temperature. Owing to the reduction of temperature of the water in the bulb, a portion of the gas in the bulb and tube was absorbed: consequently, the mercury rose in the divided tube. When the height of this column of mercury had remained stationary for about a quarter of an hour, —and the equilibrium was soon reached, if the liquid in the bulb was frequently agitated by shaking the bulb in the water-bath,— the height of the column of mercury was read off on the divided scale. The bulb was then closed, by pressing the caoutchouc joining with a screw-clamp, and removed from the rest of the apparatus by sealing it off at the narrowed part with the blow-pipe flame. The height of the barometer was then noted, the bulb weighed, and its contents analysed in exactly the same way as in the two former cases.

Determinations of the solubility of sulphurous acid in water under pressures varying between that of a few millimetres and that of three or four atmospheres, were made at each of four different temperatures, viz.: 7°C, 20°C, 39°·8C, and 50°C. The results of

these experiments are arranged in the following Tables, in which P signifies the partial* pressure under which the absorption takes place; G signifies the weight, in grammes, of sulphurous acid which one gramme of water will dissolve under the partial pressure P; and V signifies the volume of gas, in cubic centimetres, which 1 grm. of water will dissolve under the partial pressure P.

For every temperature, two Tables are given. The direct experimental results are found in the first of each of these. Column II contains the weight of sulphurous acid absorbed by 1 grm. of water under the corresponding partial pressure arranged in Column I; Column III contains the weight of sulphurous acid which, according to each experiment, would have been absorbed under the standard pressure of 760 mm., upon the supposition that the amount of gas dissolved varies directly with the pressure. In Column IV is found the weight of sulphurous acid absorbed under the pressure P, calculated by means of a careful graphical interpolation from the numbers of Column II; and Column V contains the weight of sulphurous acid which, according to the graphical interpolation, would have been absorbed under a pressure of 760 mm., supposing that the gas obeyed Dalton and Henry's law. The second Table for each temperature contains a complete series of interpolated values for regular increments of pressure, seen in Column I; Column II gives the weight of sulphurous acid absorbed under the partial pressure P; Column III contains the weight of acid which, according to the values in the second column, would have been absorbed under the pressure of 760 mm., upon the supposition that the gas obeyed the law of absorption. The columns IV and V contain the volumes of sulphurous acid (measured at 0°C and 760 mm.), corresponding to the weights in Columns II and III respectively.

* By partial pressure is meant, the total pressure under which the absorption takes place, minus the tension of aqueous vapour at the several temperatures.

Solubility of Sulphurous Acid in water at 7°C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
27·0	0·010	0·273	0·010	0·273
49·8	0·015	0·224	0·015	0·224
89·6	0·025	0·208	0·025	0·208
133·7	0·035	0·196	0·035	0·199
239·0	0·059	0·189	0·059	0·189
741·8	0·173	0·177	0·172	0·177
757·1	0·174	0·174	0·176	0·176
770·8	0·178	0·176	0·179	0 176
986·3	0·228	0·175	0·226	0·174
1291·0	0·293	0·172	0·293	0·172

Solubility of Sulphurous Acid in water at 7°C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760	V. at P.	V. at 760.
30	0·010	0·263	3·634	92·06	400	0·096	0·182	33·51	63·65
40	0·013	0·242	4·451	84·55	450	0·107	0·181	37·44	63·25
50	0·015	0·223	5·129	77·95	500	0·118	0·180	41·42	62·94
60	0·017	0·218	6·024	76·28	550	0·130	0·179	45·31	62·60
70	0·020	0·213	6·868	74·55	600	0·141	0·178	49·20	62·32
80	0·022	0·210	7·743	73·55	650	0·152	0·178	53·10	62·09
90	0·025	0·208	8·598	72·62	700	0·163	0·177	56·98	61·86
100	0·027	0·205	9·421	71·60	750	0·174	0·176	60·88	61.69
120	0·032	0·201	11·09	70·20	760	0·176	0·176	61·65	61·65
140	0·036	0·197	12·71	69·00	800	0·185	0·176	64·74	61·50
160	0·041	0·195	14·34	68·15	850	0·196	0·175	68·57	61·30
180	0 046	0·193	15·97	67·40	900	0·207	0·175	72·41	61·15
200	0·050	0·191	17·59	66·83	950	0·218	0·175	76·25	61·00
220	0·055	0·190	19·19	66·30	1000	0·229	0·174	80·01	60·88
240	0·059	0·188	20·79	65·84	1050	0·240	0·174	83·97	60·77
260	0·064	0·187	22·40	65·44	1100	0·251	0·174	87·80	60·65
280	0·069	0·186	23·99	65·10	1200	0·273	0·173	95·45	60·45
300	0·073	0·185	25·59	64·81	1300	0·295	0·172	103·00	60·25
350	0·085	0·184	29·55	64·16					

Solubility of Sulphurous Acid in water at 20° C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
32·4	0·006	0·148	0·006	0·148
50·1	0·009	0·138	0·009	0·138
65·0	0·011	0·133	0·011	0·133
77·3	0·013	0·127	0·013	0·129
78·4	0·013	0·129	0·013	0·129
82·2	0·014	0·126	0·014	0·126
121·8	0·020	0·113	0·019	0·121
291·0	0·043	0·111	0·043	0·117
446·6	0·064	0·109	0·064	0·108
658·2	0·094	0·108	0·091	0·105
728·9	0·100	0·104	0·100	0·104
729·5	0·100	0·104	0·100	0·104
730·8	0·100	0·104	0·100	0·104
1570·0	0·218	0·105	0·214	0·104
1911·0	0·260	0·104	0·260	0·104

Solubility of Sulphurous Acid in water at 20° C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760	V. at P.	V. at 760.
40	0·007	0·143	2·637	50·09	300	0·044	0·111	15·34	38·87
50	0·009	0·138	3·171	48·20	350	0·050	0·110	17·66	38·35
60	0·011	0·135	3·718	47·10	400	0·059	0·109	20·56	38·10
70	0·012	0·131	4·205	45·64	450	0·064	0·108	22·37	37·77
80	0·013	0·127	4·663	44·30	500	0·071	0·107	24·67	37·50
90	0·015	0·125	5·169	43·65	550	0·077	0·106	26·93	37·20
100	0·016	0·124	5·692	43·25	600	0·083	0·105	29·14	36·90
120	0·019	0·121	6·683	42·33	650	0·090	0·105	31·39	36·70
140	0·022	0·119	7·690	41·75	700	0·096	0·105	33·62	36·50
160	0·025	0·118	8·666	41·17	750	0·103	0·104	35·94	36·43
180	0·028	0·117	9·652	40·75	760	0·104	0·104	36·43	36·43
200	0·030	0·116	10·62	40·35	800	0·110	0·104	38·32	36·40
220	0·033	0·115	11·59	40·03	1000	0·137	0·104	47·85	36·37
240	0·036	0·114	12·54	39·70	1300	0·178	0·104	62·10	36·31
260	0·038	0·112	13·45	39·30	1600	0·218	0·104	76·35	36·27
280	0·041	0·112	14·41	39·10	1900	0·259	0·104	90·53	36·21

Solubility of Sulphurous Acid in water at 39·8° C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
205·9	0·017	0·062	0·017	0·062
293·1	0·023	0·060	0·023	0·061
696·0	0·054	0·059	0·054	0·059
697·6	0·054	0·059	0·054	0·059
701·6	0·053	0·055	0·053	0·059
1565·0	0·116	0·056	0·118	0·057
2021·0	0·150	0·056	0. 150	0·057

Solubility of Sulphurous Acid in water at 39·8° C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760.	V. at P.	V. at 760
200	0·016	0·062	5·675	21·57	760	0·059	0·059	20·50	20·50
300	0·024	0·061	8·368	21·20	800	0·062	0·059	21·58	20·50
400	0·031	0·060	11·03	20·95	1000	0·077	0·058	26·84	20·40
500	0·039	0·059	13·67	20·77	1500	0·113	0·057	39·65	20·09
600	0·047	0·059	16·29	20·64	2000	0·149	0·057	52·11	19·80

Solubility of Sulphurous Acid in water at 50° C.

I.

I.	II.	III.	IV.	V.
P.	Observed.		Calculated.	
	G. at P.	G. at 760.	G. at P.	G. at 760.
191·5	0·011	0·011	0·045	0·045
664·0	0·039	0·039	0·045	0·045
1961·0	0·115	0·120	0·045	0·044

Solubility af Sulphurous Acid in water at 50° C.

II.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
P.	G. at P.	G. at 760.	V. at P.	V. at 760.	P.	G. at P.	G. at 760.	V. at P.	V. at 760.
200	0·012	0·045	4·156	15·79	800	0·047	0·045	16·43	15·60
400	0·024	0·045	8·275	15·72	1000	0·059	0·045	20·51	15·59
600	0·035	0·045	12·36	15·65	1500	0·088	0·044	30·73	15·57
760	0·045	0·045	15·62	15·62	2000	0·112	0·044	39·07	15·55

That at a temperature of 7° C., sulphurous acid is not absorbed by water in quantities directly proportional to the pressure is distinctly seen from the numbers in the third and fifth columns of the second Table for this temperature, which, instead of being equal to one another, or deviating on either side of a mean value, as they must do if Dalton's law of absorption were applicable, gradually decrease with increasing pressure. This variation from the law of absorption is also clearly seen by reference to the curve for this temperature (curve 7° Fig. 7) which graphically represents the relations expressed in Column III of the second Table, the pressures being arranged as abscissæ, and the numbers of Column III as ordinates.

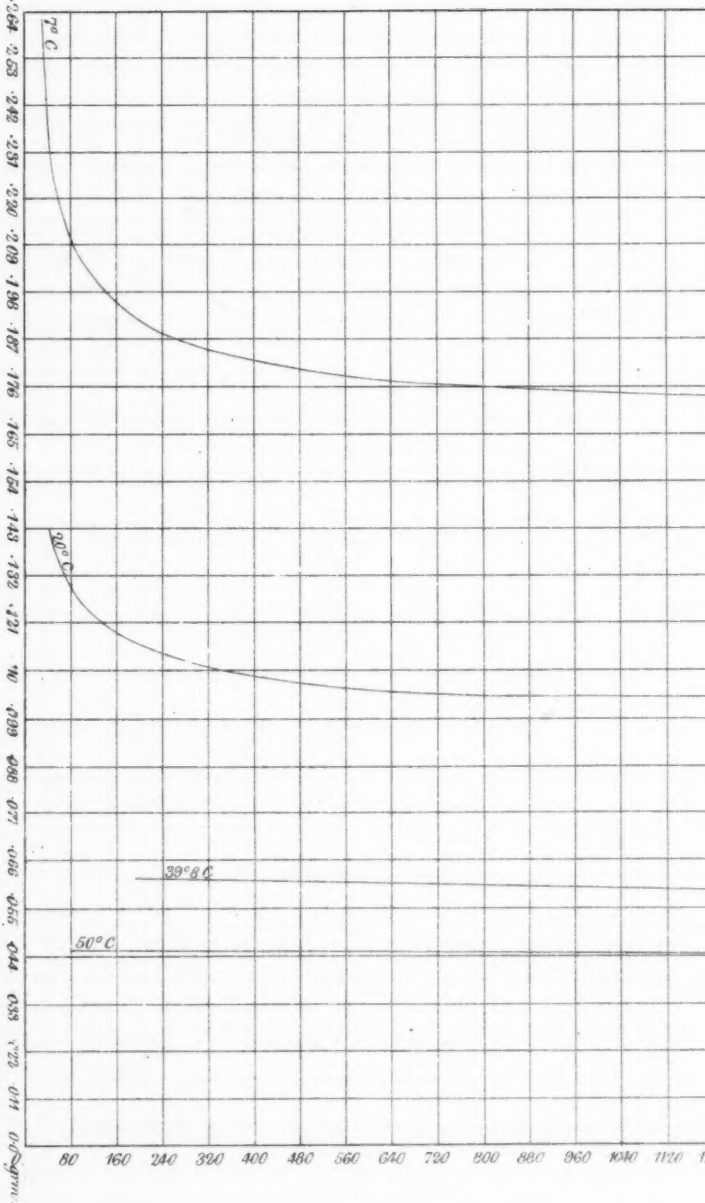
A similar examination of Columns III and V of the second of the Tables, giving the quantities of sulphurous acid absorbed at 20° C., as well as of the curve for this temperature (curve 20° Fig. 7) shows that at this higher temperature, also, the gas does not obey Dalton's law, and that the deviation, although smaller than at 7° C, is perfectly regular and perceptible. When the temperature at which the absorption occurs rises to 39°·8 C., the deviation from the law becomes still smaller, as is seen from the numbers in Columns III and V of the second Table for this temperature, as also from the corresponding curve (line 39°·8, Fig. 7) which closely approaches a straigbt line, parallel with the axis of x. At a temperature of 50° C, the quantity of sulphurous acid absorbed in water becomes directly proportional to the pressure, all variation between the several numbers in Columns III and V of the second Table, giving the experiments at this temperature, having become imperceptible. The same conclusion is arrived at by an examination of the horizontal straight line (line 50°. Fig. 7,) which gives a graphical representation of the same numbers.

From all these experiments we may therefore conclude, (I), that the deviations from the law of Dalton and Henry, which sulphurous acid and water exhibit, measured under pressures from 0·03 to 2 metres of mercury, vary according to the temperature at which the absorption occurs; and (II), that this deviation becomes less as the temperature increases, so that whilst below 40° C, the non-accordance with the law is considerable; above this temperature no variation can be perceived.

In the preceding Tables will be found the weight of gas dissolved by 1 grm. of water at each of the experimental temperatures, 7° C,

SULPHUROUS
IN WATE

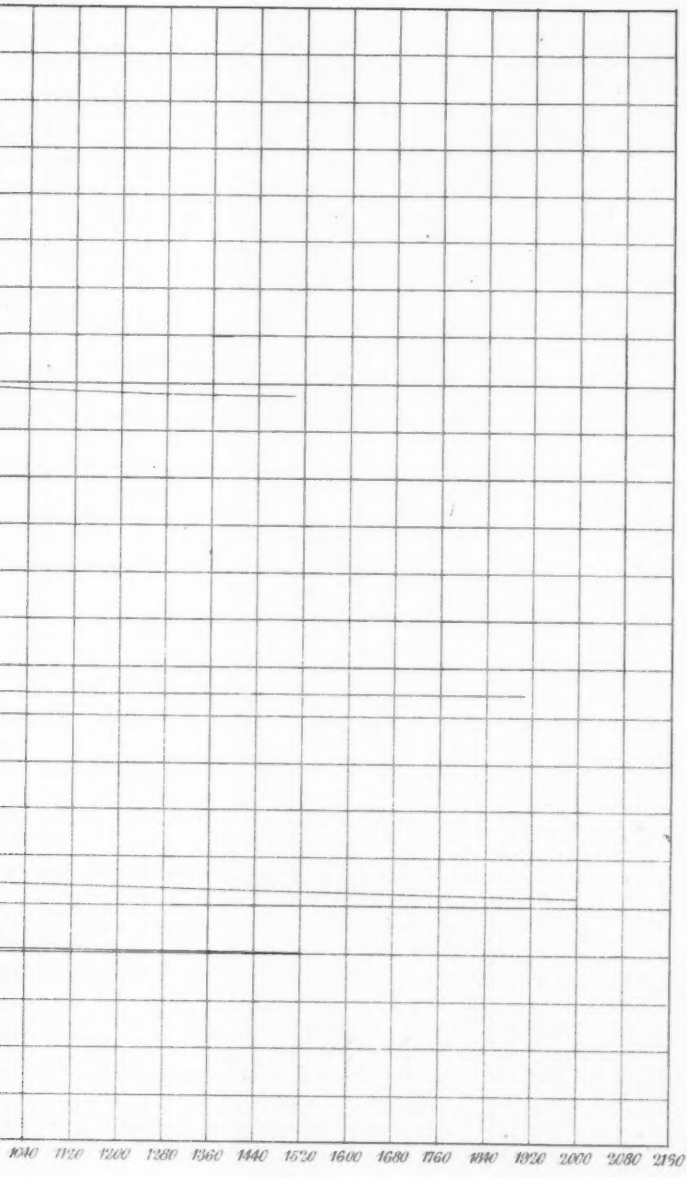
Fig. VII.



UROUS ACID

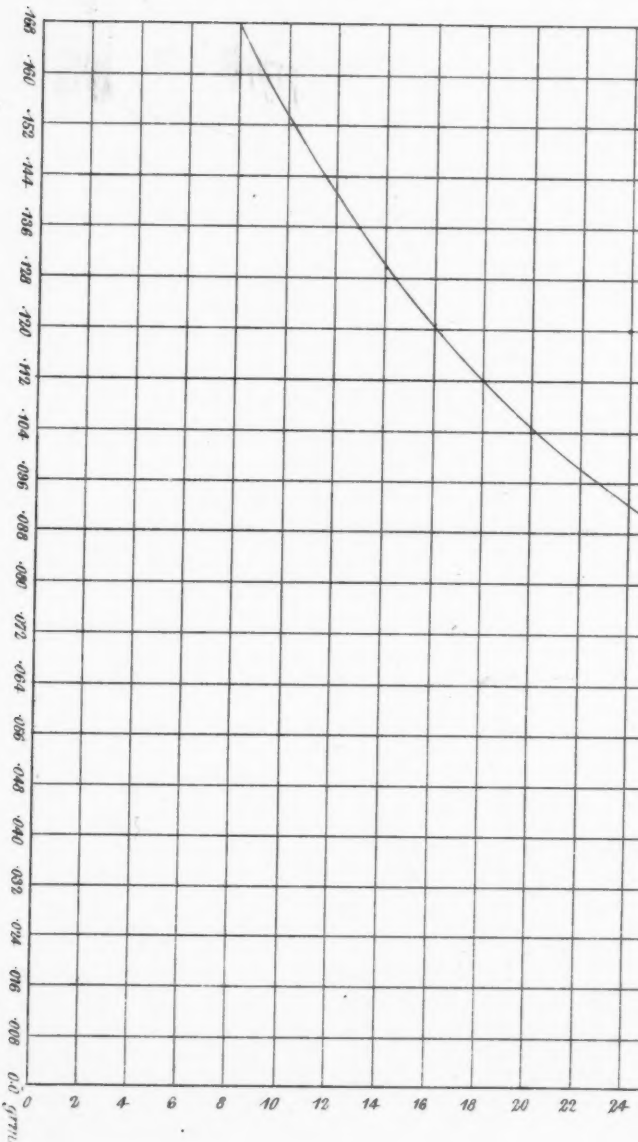
WATER.

Fig. VII.



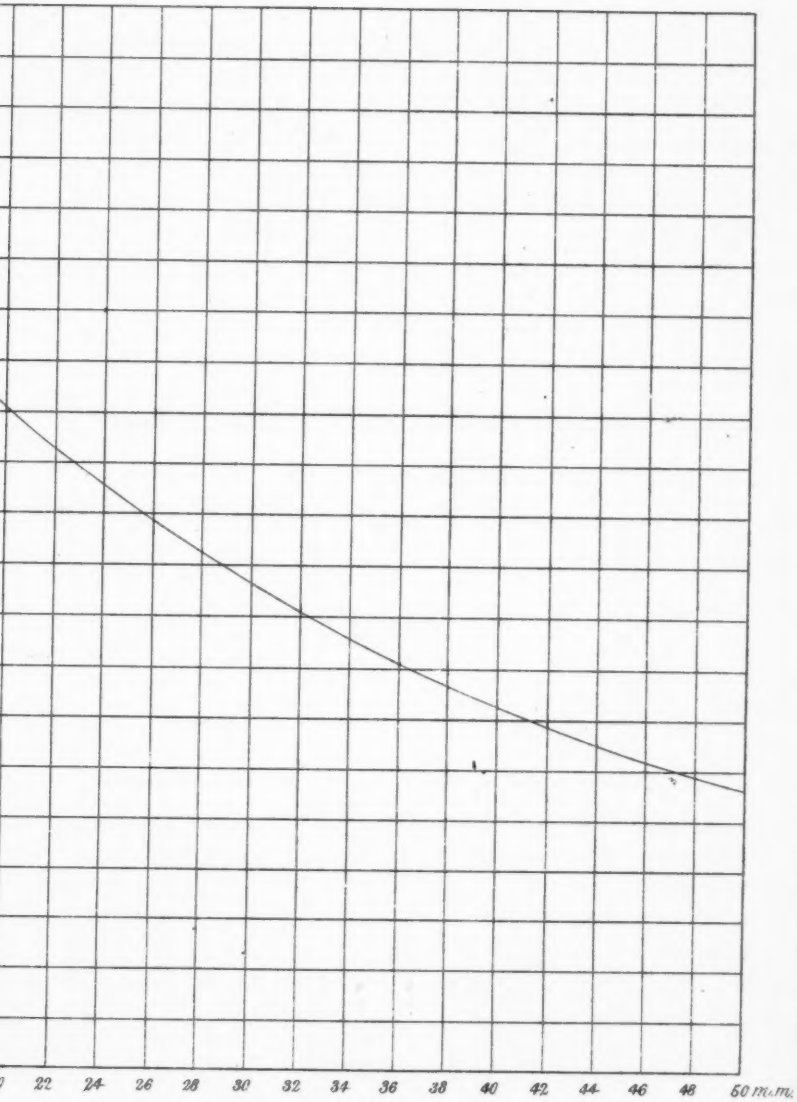
SULPHUR

Fig


0·160
0·152
0·144
0·136
0·128
0·120
0·112
0·104
0·096
0·088
0·080
0·072
0·064
0·056
0·048
0·040
0·032
0·024
0·016
0·008
0·0
0
2
4
6
8
10
12
14
16
18
20
22
24

PHUROUS ACID.

Fig. VIII.



20° C. 39°·8 C, 50° C, under a common partial pressure of 760 mm., reduced to this common pressure by interpolation of the direct observations at the several temperatures. From these values, those for the intermediate temperatures were obtained by graphical interpolation.

Column I of the following Table contains the temperatures; Column II contains the corresponding weights of sulphurous acid absorbed by 1 grm. of water; Column III contains the corresponding volumes of sulphurous acid absorbed by 1 grm. of water, all under a common partial pressure of 760 mm.

The line which represents the relation between the weight of sulphurous acid dissolved in water, under a pressure of 760 mm, and the temperature at which the absorption occurs may be seen by reference to Fig. 8.

Solubility of Sulphurous Acid in Water, at different Temperatures, under a pressure of 760 *mm. of Mercury.*

I.	II.	III.	I.	II.	III.
T°	G.	V.	T°.	G.	V.
8	0·168	58·7	30	0·078	27·3
10	0·154	53·9	32	0·073	25·7
12	0·142	49·6	34	0·069	24·3
14	0·130	45·6	36	0·065	22·8
16	0·121	42·2	38	0·062	21·6
18	0·112	39·3	40	0·058	20·4
20	0·104	36·4	42	0·055	19·3
22	0·098	34·2	44	0·053	18·4
24	0·092	32·3	46	0·050	17·4
26	0·087	30·5	48	0·047	16·4
28	0·083	28·9	50	0·045	15·6

The numbers in the above Table do not exactly agree with those formerly given by Schönfeld; the differences are, however, not more than can be easily accounted for by the employment of other methods, and by the fact that Schönfeld made his corrections for pressure dependent on Dalton and Henry's law, and that he neglected to subtract the tension of aqueous vapour from his barometric columns.

2. *Determination of the Tension of Sulphurous Acid.*

The method described, by which the absorption of sulphurous acid in water under pressures higher than the ordinary atmo-

spheric pressure is estimated, led to the following simple method of determining the tension of the vapour of liquid sulphurous acid:—

One of the tubes of liquid sulphurous acid was hermetically sealed on to the tube *e* of the apparatus C (Fig. 4). The operation of sealing these tubes together is rather a difficult one, but when once done, the joining will bear with more rough treatment than one made of a caoutchouc tube covered with brass foil, and all possibility of escape or failure is avoided. The whole apparatus was first freed from air by allowing the sulphurous acid to pass for some time through a small quantity of mercury placed in the wider tube *d* of the apparatus C (Fig. 4); the tube *d* was then filled up with mercury. The tension of the sulphurous acid at any temperature was then determined by placing the tube of liquid acid in a water-bath of the required temperature, keeping it constant at the desired point, until the level of the mercury in the tube *e* was perfectly constant, and then reading off the height of the mercury in both tubes, and observing the barometric pressure.

The necessary corrections being made for reducing the column of mercury in the tube, and that in the barometer to 0° C., the tension of the gas was equal to the column of mercury in the tube + the height of the barometer.

The following Table shows the result of two series of such determinations, the tension of the gas at each temperature being given in millimetres. The tensions corresponding to those temperatures to which an asterisk is prefixed were obtained by direct experiment, the others by graphical interpolation from the experimental numbers.

Tension of Sulphurous-acid.

Temp. in °C	Tension.			Temp. in °C.	Tension.		
	I.	II.	III.		I.	II.	III.
*0°	1162·1	1162·2	1165·1	* 8°	1596·0		
1	1209·0			* 9	1655·4	1656·7	
2	1254·0			*10	1724·5	1720·3	1719·5
*3	1310·4	1309·7		*11	1790·8	1791·0	
4	1364·0			12	1862·0		
*5	1421·0	1421·3	1421·1	*13	1926·8	1930·1	
6	1473·0			14	2003·0		
*7	1531·4	1535·0		*15	2067·7	2072·3	2064·9

Since these experiments were made, Regnault has published* a series of determinations of the tension of the vapour of sulphurous acid. The close agreement of Regnault's numbers found in Column III of the above Table with the results of my own experiments in Columns I and II, may serve as a proof of the exactitude of the simple method which I have employed.

The results of the foregoing Tables are approximately given by the following formula, which was kindly furnished me by Prof. Clifton:—

$$\text{G at } 760 = \frac{2540}{t} - \frac{9205}{t^2} + \frac{100}{P}\left(\frac{10338}{t^2} - \frac{62760}{t^3}\right).$$

where G and P retain their former signification, and t represents the temperature in degrees centigrade.

The following Table shows the close agreement of the results calculated from this formula and those obtained by direct experiment:—

P	7°C.		20°C.		40°C.		50°C.	
	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
40·0	0·245	0·242	0·149	0·143				
50·0	0·231	0·223	0·140	0·138				
100·0	0·203	0·205	0·122	0·124				
200·0	0·189	0·191	0·113	0·116	0·061	0·062	0·049	0·045
500·0	0·181	0·180	0·108	0·107	0·059	0·059	0·049	0·045
800·0	0·175	0·176	0·108	0·104	0·058	0·059	0·048	0·045
1000·0	0·178	0·174	0·106	0·104	0·058	0·058	0·048	0 045
1200·0	0·177	0·173	0·105	0·104	0·058	0·057	0·048	0·045
1800·0			0·105	0·104	0·058	0·057	0·048	0·044
2000·0			0·105	0·104	0·058	0·057	0·048	0·044

3. *Ammonia in Water.*

The experiments made by Professor Roscoe and Mr. Dittmar, on the absorption of ammonia† in water prove that, at the temperature of 0°C., this gas does not obey Dalton and Henry's law of pressures. Since all their experiments with this gas, under various pressures, were made at a temperature of 0°C. (those made at higher temperatures being all under the ordinary atmospheric pressure), I was induced to extend the enquiry to pressure expe-

* Comptes Rendus, tome, l. p. 1063. 11 Juin, 1869.

† Chem. Soc. Qu. J., vol. xii, p. 128.

riments at higher temperatures, in order to determine whether ammonia, like sulphurous acid, was dissolved at higher temperatures more nearly in accordance with Dalton's law of absorption.

The temperatures which were selected for experiment were 20°C., 40°C., and 100°C. Before commencing these determinations, I made several experiments at 0°C.; but, finding that my results corresponded sufficiently with those obtained by Messrs. Roscoe and Dittmar, I was satisfied to take their numbers as expressing the solubility of ammonia under various pressures at 0°C. The experiments made with ammonia were conducted in a way exactly similar to that employed for the sulphurous acid, at least under pressures equal to, and less than that of the atmosphere. As source of ammonia gas, a mixture of about equal weights of chloride of ammonium and slacked lime was used, the gas, before entering the absorption-bulbs, being well washed by passing through a series of bulbs containing water. In the experiments made under pressures greater than that of the atmosphere, the water in the bulb-apparatus, after being attached to the tube *e* of the apparatus C (fig. 4), was saturated with ammonia at a temperature of about 20°C.; the limb next the flask in which the ammonia gas was generating was then sealed off, the other limb still remaining connected with the tube *e* of the apparatus C by a sheet-caoutchouc joining covered with brass-foil. The bulb and contents were then gradually heated up to the temperature at which the determination was to be made, the necessary quantity of mercury, according to the pressure required, being introduced into the wider tube *d* of the apparatus *c* (fig. 4.) When the bulb had remained in the bath at the required temperature for some length of time, and the height of the mercury in the tube *e* remained constant, the bulb was closed in the usual way, and the ammonia contained in it was determined by analysis in the following manner:—The bulb, after being weighed, was broken in a beaker-glass under water containing a known volume of a standard hydrochloric acid solution, the strength of which had been accurately determined, according to Gay Lussac's well-known volumetric method, with pure silver. Care was taken to have more hydrochloric acid present than was necessary to neutralise the ammonia in the bulb, the excess of acid being determined by the addition, from a burette, of a standard soda solution, until the litmus was rendered blue.

The following Table contains the direct results of experiments made under various pressures at each of the temperatures 0° C.,

20° C, 40° C, 100° C. P signifies the partial pressure on the gas in millimetres; and G signifies the weight in grammes of ammonia absorbed at the various temperatures by one gramme of water under the pressure P. Column III in this Table, for each temperature, contains the weight in grammes of ammonia which one gramme of water will dissolve, reduced from the numbers found in Column II, to a common pressure of 760 mm., on the supposition that the gas is dissolved in quantities directly proportional to the pressure. For the temperature 0°C., the results in the Table, marked with an asterisk, were taken from Messrs, Roscoe and Dittmar's paper, in order to complete the series at 0°C. The results at the other pressures agreeing so nearly with those of these chemists, that it was not considered necessary to make a complete series of determinations at this temperature.

Solubility of Ammonia in Water.

I.

P.	0° C.		P.	20° C.	
	G at P.	G at 760.		G at P.	G at 760.
I.	II.	III.	I.	II.	III.
20·7	0·034	3·101	45·5	0·100	1·666
*97·0	0·274	2·147	206·1	0.236	0 871
*241·0	0·463	1·460	735·4	0·508	0·525
*452·0	0·652	1·096	1525·0	0·811	0·404
749·6	0·888	0·900	2076·0	1·018	0·373
757·7	0·900	0·903			
*1963·0	2·137	0·827			

P.	40° C.		P.	100° C.	
	G at P.	G at 760.		G at P.	G at 760.
I.	II.	III.	I.	II.	III.
75·8	0·050	0·497	688·4	0·067	0·074
184·3	0·112	0·461	1078·0	0·104	0·073
701·1	0·322	0·349	1419·0	0·135	0·073
1599·0	0·522	0·248			
2129·0	0·599	0·214			

The following Table contains a series of interpolated values for the several temperatures, which were obtained by measurement, from the graphic representations of the direct observations, made at each of the temperatures 0° C., 20° C., 40° C., and 100° C., which are contained in the preceding Table.

Solubility of Ammonia in Water.

II.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
P.	0°C.		20°C.		40°C.		100°C.	
	G. at P.	G. at 760.	G. at P.	G. at 760.	G. at P.	G. at 760.	G. at P.	G. at 760.
20	0·082	3·113						
30	0·117	2·960						
40	0·148	2·820						
60	0·199	2·522	0·119	1·513				
80	0·240	2·280	0·141	1·337	0·052	0·497		
100	0·280	2·127	0·158	1·200	0·064	0·490		
120	0·316	2·000	0·173	1·095	0·076	0·483		
140	0·346	1·880	0·187	1·017	0 088	0·476		
160	0·375	1·780	0·202	0·962	0·099	0·470		
180	0·398	1·684	0·217	0·918	0·109	0·462		
200	0·421	1·598	0·232	0·881	0·120	0·455		
250	0·472	1·434	0·266	0·810	0·145	0·440		
300	0·519	1·315	0·296	0·750	0·168	0·426		
350	0·563	1·223	0·325	0·705	0·191	0·414		
400	0·606	1·152	0·353	0·670	0·211	0·402		
450	0·650	1·100	0·378	0·638	0·232	0·392		
500	0·692	1·052	0·403	0·612	0·251	0·382		
550	0·732	6·012	0·425	0·587	0·269	0·372		
600	0·770	0·975	0·447	0·566	0·287	0·363		
650	0·809	0·946	0·470	0·550	0·304	0 355		
700	0·850	0 923	0·492	0·534	0·320	0·347	0·068	0·074
750	0·891	0·903	0·514	0·521	0·335	0·339	0·073	0·074
760	0·899	0 899	0·518	0·518	0·338	0·338	0·074	0·074
800	0·937	0·888	0·535	0·508	0·349	0·332	0·078	0·074
850	0·980	0·876	0·556	0·497	0·363	0·325	0·083	0·074
900	1·029	0·869	0·574	0·485	0·378	0·319	0·088	0·074
950	1·077	0·862	0·594	0·475	0·391	0·313	0·092	0·073
1000	1·126	0·855	0·613	0·466	0·404	0·307	0·096	0·073
1050	1·177	0·852	0·632	0·457	0·414	0·300	0·101	0·073
1100	1·230	0·850	0·651	0·450	0·425	0·294	0·106	0·073
1150	1·283	0·848	0·669	0·442	0·434	0·287	0·110	0·073
1200	1·336	0·846	0·685	0·433	0·445	0·282	0·115	0·073
1250	1·388	0·844	0·704	0·428	0·454	0·276	0·120	0·073
1300	1·442	0·843	0·722	0·422	0·463	0·271	0·125	0·073
1350	1·496	0·842	0·741	0·417	0·472	0·266	0·130	0·073
1400	1·549	0·841	0·761	0·413	0·479	0·260	0·135	0·073
1450	1·603	0·840	0·780	0·409	0·486	0·255		
1500	1·656	0·839	0·801	0 406	0·493	0·250		
1600	1·758	0·835	0·842	0·400	0·511	0·242		
1700	1·861	0·832	0·881	0·394	0·530	0·237		
1800	1·966	0·830	0·919	0·388	0·547	0·231		
1900	2·070	0·828	0·955	0·382	0·565	0·226		
2000			0·992	0·377	0·579	0·220		
2100					0·594	0·215		

From the graphical representations of the values at the several temperatures, the experiments for each temperature were reduced to a common pressure of 760 mm. These values will be found in the preceding Table: from them the numbers contained in Column II of the following Table, which are the weights in grammes of ammonia absorbed by one gramme of water under a pressure of 760 mm., at the several temperatures in Column I, were obtained by graphical interpolation.

Solubility of Ammonia in Water at different temperatures, under a pressure of 760 *mm, of Mercury.*

I.	II.	I.	II.
0° C	0·899	52° C	0·274
2 „	0·853	54 „	0·265
4 „	0·809	56 „	0·256
6 „	0·765	58 „	0·247
8 „	0·724	60 „	0·238
10 „	0·684	62 „	0·229
12 „	0·646	64 „	0·220
14 „	0·611	66 „	0·211
16 „	0·578	68 „	0·202
18 „	0·546	70 „	0·194
20 „	0·518	72 „	0·186
22 „	0·490	74 „	0·178
24 „	0·467	76 „	0·170
26 „	0·446	78 „	0·162
28 „	0·426	80 „	0·154
30 „	0·408	82 „	0·146
32 „	0·393	84 „	0·138
34 „	0·378	86 „	0·130
36 „	0·363	88 „	0·122
38 „	0·350	90 „	0·114
40 „	0·338	92 „	0·106
42 „	0·326	94 „	0·098
44 „	0·315	96 „	0·090
46 „	0·304	98 „	0·082
48 „	0·294	100 „	0·074
50 „	0·284		

By a comparison of the Tables of the absorption of sulphurous acid in water with those of ammonia, it is evident that at low temperatures neither of these gases is absorbed directly as the pressure: for the observed amounts dissolved, under low pressures, at low temperatures, are much larger than the calculated amounts reduced from the observed amounts dissolved under ordinary pressures, at the same temperatures, to the several

low pressures at which determinations were made, on the supposition that the gases obeyed Dalton and Henry's law.

From the preceding Tables it may also be seen that both gases, as the temperature increases, become gradually absorbed in quantities more nearly directly proportional to the pressure. At a temperature of 50° C, sulphurous acid appears to be absorbed quite in accordance with the law; whilst ammonia appears to obey the law at 100° C. A graphical representation of the pressure experiments made upon ammonia at different temperatures will be found on reference to Fig. 9.

The lines in Fig. 9, it must be noticed, represent the relation between the pressures and the numbers obtained by reducing the observed volumes of gas dissolved under the several pressures to a common pressure of 760 mm., on the supposition that the gas obeyed Dalton and Henry's law. Fig. 10 gives the line which represents the relation between the temperature, and the weight of ammonia absorbed, under a pressure of 760 mm.. by one gramme of water.

II.—*On Sugar in the Urine.*

By H. Bence Jones, M.D., F.R.S.

Part 1. *On the detection of Sugar when added to Healthy Urine.*

The detection of small quantities of sugar in water and in a solution containing organic and inorganic substances, constitute two questions as different as the detection of small quantities of arsenic or opium when dissolved in pure water or in a compound fluid.

Nothing is easier than to determine the presence of small quantities of sugar, arsenic, or opium in distilled water; but when organic matters are also present, the difficulty of the analysis becomes sometimes excessive. Very small quantities cannot be detected. The limit that can be found varies with each substance, according to the nature and amount of the organic matter present, according to the process of separation used, and according to the skill of the chemist.

In cases of poisoning, the separation of the poison from the contents of the stomach, or from the substance of the different

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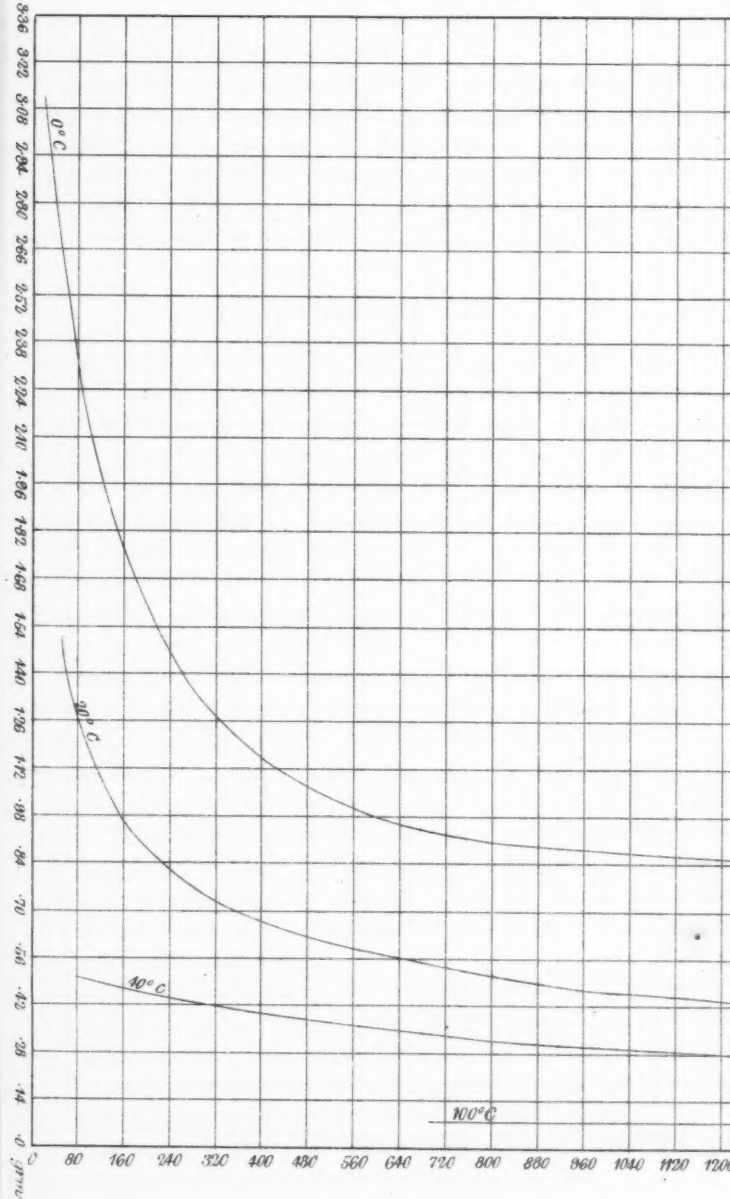
AMMONI

IN WATER

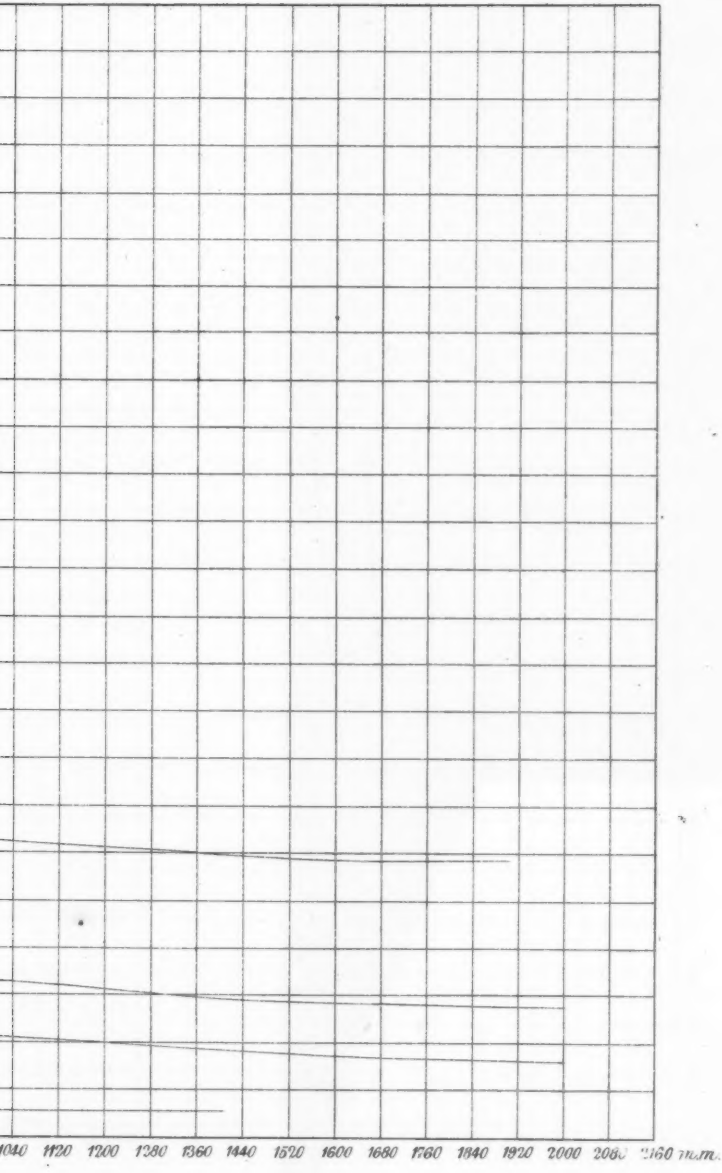
Fig IX.



M O N I A

WATER

Fig IX.



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616
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528
484
440
396
352
308
264
220
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044
0
4
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12
16
20
24
28
32
36
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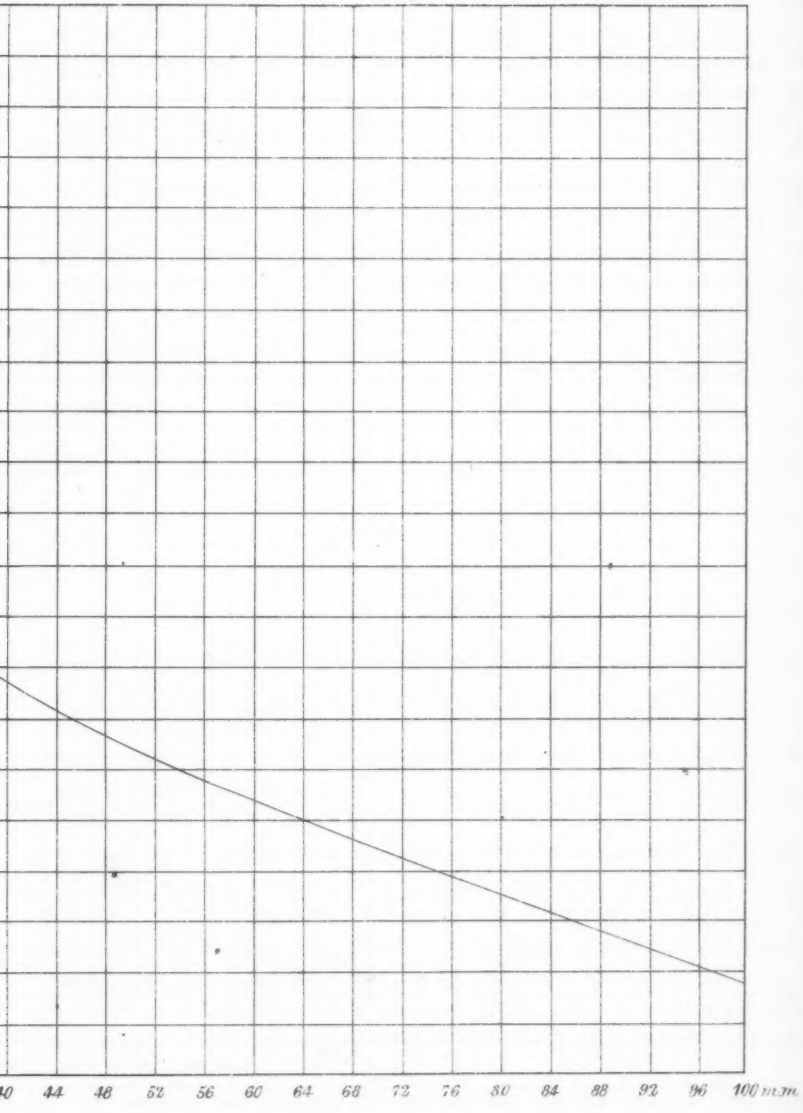
44
48

A M M O N I A.

Fig. X.



organs of the body, constitutes the whole difficulty; and this is also true regarding the detection of sugar. Whatever process is used for separating the sugar and the organic matter, some difficulties will be met with, and some limit to the quantity of sugar that can be detected will be found.

It is the object of the first part of this paper to show the difficulties and limits which exist when Lehmann's process for detecting sugar in the urine, or the fermentation process, or Soleil's Saccharimeter, or Brücke's processes are used.

I am much indebted to Drs. Ulrich and Valentine for carrying out my wishes, and for making the results as trustworthy as possible.

Lehmann's Process.

In his "Physiological Chemistry" (Translation, p. 285, vol. i), Lehmann says, "If a specimen of urine contain very little sugar, it is advisable to extract the solid residue with alcohol, to precipitate the sugar by the alcoholic solution of potassa, to dissolve the compound of sugar and potassa in water, and then to apply the sulphate of copper test."

Some experiments were first made on the solubility of potass-sugar in alcohol of different strengths.

200 c. c. of alcohol were made of three different degrees of strength, 90°, 80°, 70°, and the same amount of grape sugar was added to each. The rotation was found, by the saccharimeter, to be between 8° and 9°; the temperature was 18 C. (64° F.) The sugar was precipitated by potassa, washed with absolute alcohol, and dissolved in water; and the solutions were neutralised with hydrochloric acid, evaporated, decolorised, and examined by the saccharimeter. The alcohol of 90° then gave 4° of rotation. The alcohol of 80° gave 2° of rotation. The alcohol of 70° gave no rotation.

A similar experiment was repeated with an amount of sugar which gave 11° to 12° rotation. The alcohol of 90° gave 6° of rotation. The alcohol of 80° gave 4½°.

1 grn. of pure grape-sugar was dissolved in 50 c. c., in 100 c. c., and in 150 c. c., of an alcohol between 80° and 90°, and potassa dissolved in alcohol of the same strength was added to each solution. In each a precipitate fell, but, after standing many hours, it was scarcely perceptible at the bottom of each glass.

1 grn. of sugar in 300 c. c. of alcohol between 80° and 90°, gave a scarcely perceptible precipitate with potass-alcohol.

On the other hand, the whole of the sugar was precipitated when 6 grns. of sugar were dissolved in 200 c. c. of methylated alcohol of 99°; and when 3 grns. were dissolved in 150 c. c. of alcohol of 98° to 100° treated with potassa, and the sugar-potassa determined by the saccharimeter, the whole was regained.

These experiments show that the evaporation of the urine must be carried nearly to dryness in order that the residue may be treated with nearly absolute alcohol. It was therefore necessary to determine the effect of the evaporation on the sugar added to the urine. Known quantities of sugar were added to urine before and after evaporation.

1000 c. c. of urine were evaporated; 6 grns. of sugar were then added to the residue, which was extracted with alcohol 98°, and ultimately 3 grns. of sugar were recovered.

325 c. c. of urine, treated the same way with 8 grns. of sugar gave 5½ grns. A second experiment gave the same result.

If to 100 c. c. of urine 8 grns. of sugar were added, and the evaporation in the water-bath was carried to dryness; 5 grns. were recovered by extraction with alcohol.

A second experiment gave the same result.

When the same quantity of sugar was added to 500 c. c., 4 grns. were recovered.

If to 500 c. c. urine 15 grns. were added, between 7 and 8 were recovered after evaporation.

In 1000 c. c., when 8 grns. of sugar were added, only 2 grns. were recovered. When the same quantity was added to 2000 c. c., a trace only was detectable.

Hence, during evaporation of small quantities of urine, there is but little decomposition of the sugar that is added; but when large quantities of urine are evaporated in the water-bath, much sugar is lost; and Lehmann's process for detecting small quantities of sugar in the urine is not sufficiently delicate.

On the Fermentation Test.

Of all the tests for sugar, the most conclusive, when it can be obtained, is the production of carbonic acid and alcohol by yeast.

The following points were examined:—1. Whether equal quantities of yeast give off equal quantities of carbonic acid,—that is, whether any error arises from deducting the quantity of carbonic

acid given off by the yeast itself from the quantity given off by the yeast and sugar together? 2. What is the least quantity of sugar in water and urine that can be detected? 3. What effect urea, oxalate of urea, and the residue of the urine have on the process of fermentation? 4. What is the delicacy of the test as compared with the saccharimeter and Fehling's solution?

1. On the carbonic acid given off by yeast washed once with water:—

324·28 grns. of yeast gave 1·57 carbonic acid = 0·42 grns. per cent.
421·50 „ „ 1·79 „ = 0·48 „

In second experiment,—

240·70 grns. of yeast gave 0·75 carbonic acid = 0·31 per cent.
321·47 „ „ 1·00 „ = 0·31 „

2. What is the least quantity of sugar in water and urine that can be determined?

Half a grn. of grape-sugar with 29·99 grns. yeast, gave 0·39 grn. carbonic acid.

33·08 grns. yeast without any sugar being added gave 0·16 grn. carbonic acid.

Therefore 29·99 grns. yeast gave 0·14 grn. carbonic acid.

Hence, half a grn. of sugar gave 0·39 − 0·145 grn. carbonic acid = 0·24.

Theoretically = 0·24.

In a second experiment, after the yeast had been well washed to remove every trace of alcohol, the following numbers were obtained:—

Half a grn. of sugar, with 40·58 grns. of yeast, gave 0·34 carbonic acid.

Without sugar, 52·27 grns. of yeast gave 0·06 ∴ 40·58, give ·046.

Hence, half a grn. of sugar gave 0·34 − 0·05 = 0·29 carbonic acid.

The residue, after fermentation, was put into the smallest possible retort, and heated to boiling. The first drops that came over were tested for alcohol thus:—To one cubic centimetre of a moderately strong solution of bichromate of potassa, two or three drops of concentrated sulphuric acid were added, and then a few drops of the liquid supposed to contain alcohol. Heat was then gently used, and the fluid immediately became green from the alcohol present.

Hence, half a grn. of sugar in water gives carbonic acid that can be weighed and alcohol that can be detected.

One grn. of sugar was then added to 6 cubic centimetres of urine, and this fluid, without concentration, was fermented, and the sugar was detected. But if 1 grn. of sugar was added to 50 c. c. of urine, and this evaporated to 5 or 6 c. c., no fermentation occurred on the addition of yeast; neither was any fermentation observed when two or three grains of sugar were added.

If 3 grns. of sugar were added to 30 c. c. of urine, and this evaporated to 20 c. c,, the fluid quickly fermented, and the loss of weight was nearly the theoretical quantity.

The effect of urea and of oxalate of urea* was then determined.

The same sugar-solution was fermented without urea and with a small quantity of urea.

	Without Urea.		With Urea.
	1st Exp.	2nd Exp.	
Apparatus with sugar solution and yeast	1493·10	1506·63	1402·60
„ without „ „ „	1340·30	1351·60	1286·48
Yeast	152·80	155·03	116·12
Apparatus before fermentation . .	1493·10	1606·63	1402·60
„ after „ „	1472·26	1485·73	1381·64
Carbonic acid given off	20·84	20·90	20·96

Hence, the presence of the urea did not affect the fermentation.

If a concentrated solution of urea was taken, and 3 grns. of sugar were added to 6 c. c. of solution, no trace of fermentation occurred.

When 4 grns. of oxalate of urea were added to 34·6 grns. of sugar in solution, fermentation proceeded; but if much oxalate of urea was present, fermentation was stopped.

	4 grns. of Oxalate of Urea.	Much oxalate.
Apparatus with oxalate of urea and yeast	1618·90	1416·23
„ without „ „ „ .	1400·62	1295·08
Yeast	218·28	121·15
Apparatus before fermentation . .	1618·90	1416·23
„ after „ . .	1603·76	1415·20
Carbonic acid given off	14·94	1·03
Carbonic acid given off by yeast alone .		1·00

* Experiments were made with oxalate of urea, because this substance existed in the fermenting fluid when the urea was chiefly removed by oxalic acid added to the concentrated urine.

Hence, with much oxalate, the fermentation was almost entirely stopped.

On the comparison of the delicacy of the Fermentation-test, and with Fehling's standard solution.

A watery solution of grape sugar was prepared which gave a solution of 104°=2·288 grains of sugar in each cubic centimetre.* 15 c. c. of this solution=34·25 grains of sugar were fermented with yeast that had been once washed. A second experiment was made with the same quantities, and a third experiment was made to determine the carbonic acid in the yeast :—

	1st Experiment.	2nd Experiment.	3rd Experiment.
Yeast employed .	263·90	270·66	210·15
Carbonic acid given off	18·29	18·70	0·62
Carbonic acid in yeast	0·76	0·78	
Carbonic acid in sugar	17·53	17·92	
Hence sugar in each c.c. of solution	=2·376 grains	=2·437 grains	

10 c. c. of the same solution were diluted to 160 c.c., and tested by fresh prepared Fehling's solution.

10 c. c. of Fehling's solution were reduced by 5·6 c. c. of the diluted sugar solution.

Hence 10 c. c. of the solution before dilution contained 21·9 grains sugar, and each c. c. contains 2·192 grains sugar.

Hence in each cubic centimeter of the solution there were present :—

By fermentation, 2·371 and 2·437 grs. sugar mean	=2·356 grs.
By saccharimeter	2·288 grs.
By copper test	2·192 grs.

On Soleil's Saccharimeter.

Before the saccharimeter can be used, the fluid about to be examined must be decolorised. To effect this, animal charcoal, acetate or subacetate of lead and ammonia, or chlorine gas must be used. These substances, whilst removing the colour, keep back or destroy some of the sugar, and it was desirable therefore to determine the loss.

* This number is obtained by making a solution of sugar which contains .01 gramme of sugar in each cubic centimetre when examined by Fehling's solution. This amount of sugar in solution gives seven degrees of rotation.

First, charcoal:—A colourless solution of sugar which gave 7° of rotation was mixed with animal charcoal, boiled for a few minutes, and left for a few minutes longer, before it was filtered. The charcoal was washed three or four times with hot water. The washings were added to the fluid which first came through, and the whole was then found to give the same rotation as at first.

A fluid, dark brown from the colouring matter of the urine had three grains of sugar added to it, and it was then mixed with animal charcoal; after standing some time, it was filtered, and as it was not colourless, it was again treated with animal charcoal, and this was repeated a third time. The animal charcoal was many times washed with hot water. The clear fluid ultimately obtained was examined by the saccharimeter, and the loss was found to be not more than the frequent filtrations might account for.

A colourless solution of sugar in water gave between 9 and 10° of rotation. 75 c. c. of this solution were shaken with a small quantity of purified and fresh-burnt animal-charcoal, the fluid was then filtered, and the charcoal was not washed. The solution then gave between 7° and 8° of rotation.

75 c. c. of the same solution with twice the quantity of animal charcoal gave a rotation between 5° and 6°.

75 c. c. of the same solution with three times the quantity of animal charcoal, gave a rotation of between 4° and 5°.

One volume and a half of the same sugar-solution was mixed with one volume of animal charcoal. The clear fluid which passed through the filter was found to have lost half its rotating power.

It follows from these experiments, that a large excess of animal charcoal retains much sugar, and that the more charcoal used the less sugar passes through the filter; but all the sugar that is kept back can be washed out with boiling water.

It was desirable to know how much charcoal could be used without perceptible loss of sugar. 50 c. c. of a pure solution of sugar gave 27° of rotation. It was mixed with between 55 and 60 grains of charcoal shaken and filtered, and then gave 26°.

25 c. c. of a nearly colourless diabetic urine were diluted to 55 c. c.; the rotation was then between 15° and 16°. 50 c. c. of the same urine, shaken with 60 grs of charcoal, gave a colourless solution which rotated between 31° and 32°.

Some experiments were made with wood-charcoal to see its effects on sugar and on the colouring matter of the urine.

The wood-charcoal was finely powdered, but not fresh burnt.

One volume of pure sugar solution was shaken with half a volume of wood charcoal, and left to stand for some time. The solution gave 19° of rotation both before and after treatment. The same charcoal was shaken with urine, the fluid which filtered through was nearly as dark coloured as at first.

These experiments were repeated with fresh burnt wood charcoal. The solution of sugar was not affected. The colouring matter of the urine was partly removed, but the whole of the colour could not thus be taken away.

On the action of basic and neutral acetate of lead on solutions of sugar.

Dr. E. Robiquet, in his instructions for using his diabetometer, says that 25 c. c. of diabetic urine are to be mixed with 1 c. c. of extract of lead and 1 c. c. of liquid ammonia. The whole is to be shaken for some minutes to give a deposit. If the clear liquid is not completely decolorised, the same quantity of lead and ammonia is again to be added. If the decoloration is then complete, the amount of sugar may be determined by the amount of rotation observed.

25 c. c. of sugar-solution were diluted to 50 c. c. with water. Two experiments gave 21° and 22° of rotation. The same quantity of the same solution was mixed with 20 c. c. of neutral acetate of lead and 2 c. c. of ammonia, and the whole was diluted to 50 c. c. after filtration the rotation was found to be, in the first experiment, between 18° and 19°, and in the second experiment 18°. 25 c. c. of sugar-solution diluted to 50 c. c. gave between 9° and 10° of rotation. 25 c. c. of same solution with 2 c. c. of acetate of lead and 2 c. c. of liquid ammonia, and the whole diluted to 50 c. c. gave only 7° of rotation.

By using three times as much solution of lead and ammonia, the rotation was only 4° to 5°.

On the action of basic acetate of lead alone.

50 c. c. of urine were mixed with a solution of sugar which gave 9° of rotation; after precipitation by basic acetate of lead it was found to have lost 3° of rotation. A second experiment gave the same result.

A urine which gave between 8° and 9° of rotation gave from 5° to 6° after precipitation. The lead-precipitate was washed with hot water on the filter and boiled with hot water, but the sugar could not be removed.

In order to compare the action of basic and neutral acetate of lead on saccharine urine and on solutions of sugar in water alone, and in water with common salt and water and phosphate of soda, the following experiments were made.

A pure sugar-solution gave 10° to 11° of rotation; when mixed with common salt and precipitated by basic acetate of lead, it gave the same rotation; when more common salt was used, no difference was observed.

A solution of sugar which gave 9° of rotation was mixed with solution of common salt and urate of soda, and precipitated by basic acetate of lead; the rotation was then found to be between 7° and 8°. When the quantity of salt and urate of soda was less, the rotation was 8°.

A solution of sugar giving between 10° and 11° of rotation was mixed with much phosphate of soda, and then precipitated by basic acetate of lead: it then gave 8° to 9°.

A solution of sugar which gave 5°, after being mixed with much phosphate of soda and precipitated by basic acetate of lead, gave from 3° to 4° of rotation.

A solution giving 10° to 11°, mixed with a little urate of soda, and then precipitated by basic acetate of lead, gave 10° of rotation.

When neutral acetate of lead was used instead of basic acetate, very different results were obtained.

A pure sugar-solution gave 10° to 11° of rotation. When the solution was mixed with common salt, phosphate, and urate of soda, it gave, after precipitation, 10° to 11° of rotation, and the rotation was unchanged when a greater amount of these salts was added before precipitation.

1st. These experiments confirm the fact that a pure solution of sugar is not precipitated either by basic or by neutral acetate of lead, but that sugar is precipitated by neutral acetate of lead and ammonia.

2nd. Basic acetate of lead when added to saccharine urine causes the precipitation of some sugar. The urates and phosphates in the urine cause this precipitation of sugar, and not the chloride of sodium; for when a solution of sugar in water is mixed with chloride of sodium, basic acetate of lead causes no precipitation of the sugar. But when urate or phosphate of soda also is present, then some sugar is precipitated.

3rd. When neutral acetate of lead is added to solutions of

sugar containing chloride of sodium, phosphate, and urate of soda, no precipitate of sugar occurs.

On the action of Chlorine.

Into a solution of sugar in water containing 6 grains of sugar to 20 c.c. of water, chlorine gas free from hydrochloric acid was passed for half an hour. It was left for twenty-four hours, and then hardly any difference of rotation was observed.

Into a solution of the same strength, chlorine was passed for an hour and a half, and it then was left for twenty-four hours; the loss was less than a grain of sugar.

325 c. c. of urine were mixed with 3 grains of sugar and to 20 c. c. The concentrated fluid was heated for twenty minutes with chlorine. It had then a yellowish urine colour, which could not be removed by further exposure to chlorine, and the subsequent use of animal charcoal did not give a solution which could be examined by the saccharimeter.

Pettenkofer's Test.

The fluid in which sugar is suspected is decolorised as far as possible, and then mixed with a few drops of a concentrated solution of glychocholic acid in soda or cholalic acid. Three or four drops of concentrated sulphuric acid are then added, and the whole gently heated without boiling. If sugar is present, a purple colour is seen at the edge of the watch glass: this is more evident on a white ground.

A standard solution of grape-sugar was made, 1 c. c. containing 0·005 sugar, and 5 drops of the solution = 1 milligramme, and was mixed with cholic acid and concentrated sulphuric acid: intense purple blue immediately formed.

One drop of this solution = 0·0002 of sugar, mixed with cholic and sulphuric acid gave, after a few minutes, a slight purple red and ultimately a tinge of blue.

5 drops of diabetic urine containing 7 grs. of sugar to the ounce of urine were mixed with cholic acid, and a strong sulphuric acid. After a few minutes, a slight purple red appeared which ultimately became bluish.

One drop of this diabetic urine without decoloration gave a purple red. Cholalic acid was found to have the same reaction as cholic acid.

Trommer's Test.

Among the different ways of employing this test, that recommended by Lehmann was found to be best. By it, $\frac{1}{20}$ per cent. (or 0·24 gr. to 1 oz.) of sugar added to the urine was easily detected by deposit of suboxide of copper.

2 or 3 c. c. of urine are mixed with a few drops of potassa and filtered, and then an equal quantity of strong potassa is added, with about 3 drops of a solution of sulphate of copper; the whole is well shaken, and the clear liquid poured off from the hydrated oxide of copper which has not dissolved. If the blue solution when heated (long boiling is quite unnecessary) becomes colourless without depositing suboxide of copper, then two drops more of the sulphate of copper should be added, and the experiment repeated. A separation of suboxide is often thus obtained, provided the boiling has not been continued so long at the first heating as to decompose the sugar.

Pure grape-sugar in water gives the well-known red suboxide. In urine, the suboxide is bright yellow or dirty yellow. When 0·01 gramme of grape-sugar dissolved in water was precipitated by acetate of lead and ammonia, and the precipitate treated with a little oxalic acid solution, the sugar solution gave a dirty yellowish reduction with standard copper-solution.

A solution of grape-sugar was mixed in different proportions with a solution of chloride of ammonium. The separation of the suboxide of copper was stopped, when the solution containing $\frac{1}{200}$ of a grain of sugar also contained 1 grain of chloride of ammonium. In some experiments, the suboxide of copper was deposited whilst ammonia in quantity was being given off.

The same series of experiments were made with urea and grape-sugar: the urea hindered the separation of the suboxide, when a solution containing $\frac{4}{1000}$ of a grain of sugar contained also 1 grain of urea.

Brücke's Processes.

Professor Brücke has published two processes for detecting small quantities of sugar in urine.

In the first or alcohol process, he advises that the urine should be mixed with four times its bulk of absolute alcohol. An alcoholic solution of potassa is then to be added, and the fluid is left for twelve hours to deposit potassa-sugar. The alcohol is then to be poured off, and the deposited matter dissolved in water and tested by reduction and other tests.

According to the experiments described in the early part of this paper, when small quantities of sugar exist in solution, an alcohol of 80 per cent. will only give from one-third to a scarcely perceptible quantity of the sugar which existed in a solution. If a very small quantity of sugar was present, this percentage of alcohol would therefore fail to detect it. With absolute alcohol by this process, the whole of the sugar is precipitated, but if the percentage of alcohol falls below 80, little or no sugar will be obtained. An alcohol of 90 per cent. gives only half the sugar that is present; and hence this method of Professor Brücke is very imperfect and very costly; even with methylated spirit.

In his second process, he recommends that the urine should be precipitated with neutral acetate of lead and then with basic acetate of lead, and after filtering off the precipitate, ammonia should be added; in this last precipitate the chief part of the sugar present will be found. What is the amount of sugar which, when added to the urine, can be detected by this process?

145 c. c. of fresh morning urine were treated with acetate of lead, basic acetate of lead, and then ammonia. 5 c. c. of a standard solution of sugar containing 0·025 gramme = $\frac{1}{3}$ of a grain nearly of sugar, was added before precipitation. The solution was almost free from colouring matter after precipitation by basic acetate of lead and quite free when precipitated by ammonia.

On adding 20 drops of a standard solution of copper to the potass solution of the subacetate of lead, no red suboxide of copper formed, but a dirty suboxide of copper fell. The solution of the ammonia precipitate in oxalic acid gave only a trace of red oxide, but plenty of dirty coloured suboxide. In the cold after 24 hours the same reduction occurred.

200 c. c. of fresh morning urine were treated as in the last experiment, but only 0·012 gramme = $\frac{1}{6}$ of a grain of sugar was added. The oxalic acid solution of the ammonia precipitate gave with 10 drops of copper solution a slight reduction, a dirty yellowish precipitate was obtained on boiling. The potash solution of the subacetate of lead precipitate destroyed the blue colour of the sulphate of copper solution but gave no precipitate.

200 c. c. of fresh mid-day urine were treated as before, 0·05 gramme = $\frac{3}{4}$ of a grain of sugar was added. The three precipitates were examined as well as the solution filtered from the ammonia precipitate.

1. The acetate of lead precipitate gave no reduction.

2. The basic acetate of lead precipitate was dissolved in potassa and gave no reduction; the blue colour of the copper solution disappeared however.

3. The precipitate with ammonia was treated with solution of oxalic acid, and on the addition of 4 c. c. of standard-copper solution a good reduction was obtained of a yellowish colour.

4. The clear liquid from the ammonia precipitate gave no reaction of sugar.

200 c. c. of fresh urine were treated as before; only ·01 gramme = $\frac{1}{7}$ of grain of sugar was added. The oxalic acid solution contained as usual the whole of the sugar. 2 c. c. of copper solution gave a dirty yellowish precipitate.

When the same quantity of grape-sugar was added to distilled water and treated in the same way, the oxalic-acid solution tested by the standard copper solution gave the same dirty-yellow precipitate.

To 700 c. c. of urine a known quantity of solution of grape-sugar giving 12° of rotation of the saccharimeter was added. The urine was treated as before. The ammonia precipitate decomposed by oxalic acid, contained sufficient sugar when diluted to the known quantity to give a rotation of 8°. Instead of decomposing the ammonia precipitate by oxalic acid, sulphuretted hydrogen was used, and if requisite this was twice repeated; the filtrate is then almost colourless, even when 5000 c. c. of urine have been used for an experiment.

To 1300 c. c. of urine a known quantity of a solution of grape sugar was added, giving 13° of rotation. In the ammoniacal precipitate enough sugar was found to give between 7° and 8° of rotation.

To 1137 c. c. of urine a known quantity of sugar solution was added, giving 11° to 12° of rotation in the ammoniacal precipitate; enough sugar was found to give, with the same quantity of water, 8° to 9° of rotation. This experiment when repeated gave in the ammoniacal precipitate 8° of rotation.

Hence by Brücke's lead process, when $\frac{3}{4}$, $\frac{1}{3}$, $\frac{1}{6}$, $\frac{1}{7}$ of a grain of grape-sugar are added to about 200 c. c. of urine, decided evidence of sugar was found in the ammonia precipitate. And by the quantitative experiments it appears that about two-thirds of all the sugar added can be recovered by this process.

The results of these experiments on the detection of sugar when added to the urine may be thus summed up:

1. Lehmann's process for detecting sugar in the urine cannot be employed when small quantities of sugar are present in large quantities of urine; by evaporation and decoloration, all the sugar is lost.

2. The process of fermentation is stopped by the residue of the urine, by much urea and by oxalate of urea still more decidedly. Half a grain of sugar in water can be detected by the alcohol produced, and may be determined approximatively by the carbonic acid given off; but in concentrated urine much larger quantities will be entirely overlooked.

3. In decolorising the urine for use in the saccharimeter, sugar is always lost; animal charcoal retains sugar in proportion to the amount of charcoal used. When the urine is decolorised by basic acetate of lead and ammonia, two-thirds of the sugar may be lost.

4. Pettenkofer's test for sugar is the most delicate test known; $\frac{2}{3}$ of a milligramme in distilled water, can be detected by it, and a little colouring matter of the urine does not hinder the reaction. If much colouring matter is present, it must be removed.

5. Trommer's test is capable of discovering $\frac{1}{200}$ per cent. of sugar in the urine, but when very small quantities of sugar are in solution with hydrochlorate of ammonia or urea, the reduction of the oxide of copper is not perceived; $\frac{1}{200}$ of a grain of sugar with 1 grain of hydrochlorate of ammonia, in water, gives no reduction; and $\frac{4}{1000}$ of a grain of sugar with 1 grain of urea stopped reduction.

6. Brücke's processes.

In the alcohol process if 80 per cent. alcohol is used, only $\frac{1}{4}$ or less of the sugar is obtained: and even by 90 per cent. alcohol one-half is lost. The necessity for so much absolute alcohol as will give with the urine a mixture of 90 per cent., makes the process nearly useless.

By Brücke's lead process, the best results have been obtained; $\frac{1}{7}$ of a grain of sugar in 200 c. c. of urine could be detected, and $\frac{2}{3}$ of all the sugar added was recovered. Moreover, when sulphuretted hydrogen is used to decompose the ammonia precipitate, the sugar is obtained in a state fit for fermentation, and free from colour, so that the saccharimeter can be employed.

PART 2.—*On the detection of sugar naturally present in healthy urine.*

The presence or absence of sugar in healthy urine is not only of great interest in relation to the true comprehension of the nature of diabetes, but it is also of importance in respect to

our knowledge of the chemical changes which occur in the body in health.

If sugar exists in the urine in health, as Brücke maintains, then diabetes must be considered as an exaggeration of a healthy state, and not as a distinct and peculiar condition of the system; and it will be necessary to admit, that in health and in diabetes, the same chemical changes take place in the system, but that the greater amount of change in the one case constitutes health, and the lesser amount in the other case is called diabetes.

Professor Brücke deserves all credit for the accuracy of his observations, and for the clearness of his statements; and though I failed by the alcohol process to satisfy myself of the truth of the results which he obtained by that method, yet, by his lead process, I have fully convinced myself, after a lengthened investigation, which only the perseverance of Dr. Ulrich could have carried out, that there is sugar in healthy urine; and that, in addition to the proofs of its presence mentioned by Professor Brücke, it may be detected and measured by the saccharimeter; and that by fermentation, alcohol in recognisable quantity may be obtained.

On the detection of sugar in healthy urine, by Brücke's alcohol process.

140 c. c. and 200 c. c. of fresh urine were mixed with four times their bulk of alcohol sp. gr. 808 (or 95 per cent.), a solution of potassa in the same strength of alcohol was added, and the fluid was left for twelve hours to allow the potass-sugar to deposit itself. The liquid was then poured off; the deposited matter was dissolved in water, and tested by Trommer's test, Böttger's test, and a solution of potassa alone. No conclusive result was obtained.

Three other experiments were then made with 1,000 c. c. of urine and alcohol of the same strength. The copper test gave a decided reduction; the potassa alone hardly deepened in colour. The bismuth test was not conclusive; on testing the deposit from the alcohol for uric acid, it was found to be present in considerable quantity. In the Medico-Chirurgical Transactions vol. 26, p. 215 (1843), I have shown that uric acid reduces the oxide of copper in Trommer's test. Hence the reduction obtained in these three experiments was no proof of sugar being present, and I determined to try whether, by using large quantities of urine, sufficient sugar

could be precipitated to admit of the determination of its presence and amount by the saccharimeter.

3,000 c. c. of urine (about 5 pints) were added to 12,200 c. c. of alcohol (above 21 pints). This quantity was divided into three portions; potassa dissolved in alcohol was added to each portion before it was set aside to deposit the sugar-potassa. The precipitate was dissolved in water, neutralised with oxalic acid, filtered through animal charcoal, and concentrated on a water-bath to about one ounce (30 c. c.). The clear fluid was examined by the saccharimeter, but no trace of rotation could be observed.

In another experiment, 1,000 c. c. of fresh urine were mixed with 4,000 c. c. of alcohol, and treated in the same way; but no trace of rotation was observed.

Another series of three portions of 1,000 c.c. of urine each, was mixed with 12,000 c.c. of alcohol, sp. gr. 808. The smallest quantity of water was used for dissolving the potassa sugar; a very small quantity of animal charcoal was used for decolorising the solution, which was examined by the saccharimeter; but no rotation could be seen.

Failing thus to detect sugar by the saccharimeter, I used Pettenkoffer's test on fresh portions of urine.

200 c. c. were mixed with alcohol and treated with potassa. A very small quantity of cholalic and of cholic acids was dissolved in concentrated sulphuric acid, and some of the fluid thought to contain sugar was added, but no purple tint in either case was produced. The test failed to find sugar, though the same solutions detected 2 milligrammes of sugar (·03 of a grain) dissolved in 10 drops of water, and one drop of diabetic urine, containing ·05 grain of sugar, gave a fine purple colour. As it was possible that by using a larger quantity of urine, some trace of sugar might be found, 3,000 c. c. of urine were precipitated by alcohol. The deposit was dissolved in a very small quantity of water and decolorized by animal charcoal, but no decided evidence of sugar was obtained.

At the time when these experiments were made with the alcohol process, I did not know how little sugar was precipitated by potassa from 80 per cent. alcohol. As this process failed, the lead process was tried.

On the detection of sugar in healthy urine by Brücke's lead process.

200 c. c. of healthy morning urine, passed by A, were treated

with lead and ammonia; the basic acetate of lead precipitate was dissolved in a small quantity of potassa, and the solution was tested with Fehling's standard-copper solution; no reduction was obtained, but the blue colour of the copper solution disappeared, and the liquid became of a light amber colour, but not a trace of suboxide of copper was seen. The ammonia precipitate was treated in the cold with oxalic acid, and the filtrate was examined for sugar by the copper solution, but no reduction occurred.

200 c. c. of mid-day urine (A) were treated exactly in the same way, and with exactly the same results.

500 c. c. of healthy urine (A) treated in the same way with oxalic acid gave no decided evidence of sugar by reduction, or by Pettenkoffer's test. This experiment repeated with another quantity of urine gave the same result. When in another experiment, the ammoniacal precipitate was decomposed by sulphuretted hydrogen, decided evidence of reduction was obtained.

1,000 c. c. of same urine (A) treated with oxalic acid instead of sulphuretted hydrogen, gave a reduction which was not sufficiently distinct. When this experiment was repeated and sulphuretted hydrogen employed, a distinct reduction of the oxide of copper took place, and Pettenkofer's test also showed that sugar was there. This last experiment was three times repeated, and reduction always occurred.

1,000 c. c. of the urine of another healthy man, (B) was treated in the same way by lead and sulphuretted hydrogen; the clear filtrate was evaporated and it reduced the copper solution readily.

2,000 c. c. of the urine (A) gave a very plentiful reduction. The experiment was repeated; the filtrate from the sulphide of lead was evaporated to dryness, and extracted with absolute alcohol; potassa-alcohol was then added; and a deposit formed on standing, which gave a good reduction.

It was requisite to prove that the reduction was caused by sugar. For this purpose, larger quantities of urine were treated in the same way, and the ammonia precipitate was tested for sugar by the saccharimeter and by fermentation.

5,000 c. c. of urine (A) were examined; the filtrate from the sulphide of lead was evaporated in vacuo; and the residue dissolved in a little water was decolorised by a little animal charcoal; half the solution examined by the saccharimeter gave 4° of rotation. In two other experiments with different quantities of the urine (A), 2° and 3° degrees of rotation were observed.

5,000 c. c. of urine (B) treated in the same way gave 5° of rotation.

1,100 c. c. of the urine of a third person (C) treated in the same way, gave $1\frac{1}{2}$° of rotation; and by the reduction-test sugar was easily found.

In two experiments with 10,000 c. c. of urine (A) treated with oxalic acid, the decoloration could not be made so as to allow of the use of the saccharimeter; but the reduction-test and Pettenkofer's test gave full evidence of sugar.

Hence, in those different healthy persons, and in six different experiments, the rotation showed that sugar was present in the urine.

On the amount of rotation observed in healthy urine.

Two more experiments were made with the urine of (A) and (B), to determine the greatest amount of rotation in health.

5,000 c. c. of the urine (A) were treated as before with sulphuretted hydrogen. The whole of the fluid was used in the saccahrimeter, and the rotation was between 7° and 8°.

5,000 c. c. of the urine (B), when all the fluid was used, gave from 10° to 11° of rotation.

On the proof of the presence of sugar in healthy urine by fermentation.

10,000 c. c. (10 litres) of the urine (A) were treated with sulphuretted hydrogen. The filtrate was evaporated, and half was fermented in two portions.

	1st Portion.	2nd Portion.
Yeast employed . .	31·22 grs.	29·30 grs.
Total carbonic acid given off	0·80 gr.	0·86 gr.
Carbonic acid from yeast .	0·43 gr.	0·41 gr.
Carbonic acid from sugar .	0·37 gr.	0·45 gr.

Hence total carbonic acid from sugar = 0·82 gr. = 1·68 gr. sugar; so that the total quantity thus obtained from 10 litres was 3·36 grs. sugar.

14,000 c. c. of urine (A), after the filtrate from the sulphide of lead was evaporated to dryness, had the sugar precipitated from

absolute alcohol by potassa. The precipitate was dissolved in water, neutralised by hydrochloric acid and evaporated; the residue extracted by strong alcohol; the alcoholic solution again evaporated to dryness; and the residue again dissolved in water, mixed with yeast which had been well washed, and kept at a temperature between 25° and 30° C.: (77° and 86°) F. in half an hour it began to ferment.

Yeast employed in sugar-solution . .	34·2 grs.
Carbonic acid given off	1·8 gr.
Yeast without sugar-solution . .	109·6 grs.
Carbonic acid given off	0·3 gr.

Therefore carbonic acid in 34·2 grs. of yeast may be neglected.

The yeast alone mixed with water and distilled, gave a scarcely perceptible trace of reduction when the distillate was added to a solution of chromic acid, whereas the other yeast-mixture distilled gave a fluid which showed plentiful reduction, proving that alcohol was present after fermentation.

The total carbonic acid given off = 1·8 gr.; this corresponds to 3·7 grs. sugar obtained from 14 litres of healthy urine.

An undetermined quantity of the different fluids which had been used in the experiments with the saccharimeter was evaporated; the residue extracted with strong alcohol; the alcoholic solution evaporated; the residue again redissolved in strong alcohol; and the solution was evaporated to dryness, dissolved in water, and mixed with slightly washed yeast.

Yeast used	44·6 grs.
Carbonic acid . . .	2·4 grs.

Yeast without sugar-solution 100·3 grs.; carbonic acid 0·7 gr. Hence 44·6 yeast give 0·3 gr. carbonic acid.

Hence carbonic acid from sugar = 2·4 grs. − 0·3 = 2·1 grs. = 4·3 grs. sugar.

The fluid distilled from yeast alone reduced chromic acid; the fluid which was distilled from the other apparatus reduced the chromic acid much more decidedly.

On the determination of the amount of sugar present in healthy urine.

Although the saccharimeter and fermentation afford the most

satisfactory proof of the presence of sugar, yet the quantitative determination by either of these methods is not so accurate or so useful as by means of Fehling's standard-copper solution; because the processes for decolorising and for separating the sugar from the urine cause a great loss, which does not occur when the amount of sugar is determined by a standard solution, because then a smaller quantity of urine will give conclusive results.

1,000 c. c. (1 litre) of urine (A) was treated as before; the filtrate from the sulphide of lead was evaporated on a water-bath, decolorised with a little animal charcoal, and then tested by Fehling's solution.

The volume of fluid was 29 c. c.; of this 15 c. c. were required to reduce 10 c. c. of Fehling's solution. Hence the 29 c. c. contained 0·09 gramme sugar = 1·4 grain, as by the process one-third of the sugar present is lost. The litre contained about 2·2 grs. of sugar.

In another litre (A) the volume of fluid was 18 c. c.; of this 12 c. c. reduced 10 c. c. of Fehling's solution. Hence 18 c. c. contained 0·07 gramme sugar = 1·08 gr. Adding one-third to this, we find that the litre contained about 1·5 grains.

In another litre (A) the volume of fluid was 18 c. c.; of this 13 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·06 gramme sugar = ·924 gr. One-third added = 1·38 gr. to litre urine.

In another litre (A), the volume of fluid was 18 c. c.; of this 11 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·08 gramme sugar = 1·23 gr. One-third added = 1·8 gr. sugar to litre urine.

A litre of urine (B) was treated in the same way. The volume of fluid was 18 c. c.; of this 7 c. c. reduced 10 c. c. of Fehling's solution. Hence the 18 c. c. contain 0·13 gramme sugar = 2·0 grs. One third added = 3·3 grs. sugar to litre urine.

In another litre (B), the volume of fluid was 26·6 c. c.; of this 12·6 c. c. reduced 10 c. c. of standard solution. Hence the 26·6 contain 0·1 gramme sugar = 1·5 gr. One-third added = 2·3 grs. sugar to litre urine. By the saccharimeter also evidence of rotation was obtained.

Hence,	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.
1 litre (A) urine contained	2·2 grs.	1·54	1·38	1·8 gr. sugar.
1 litre (B) urine contained	3·0 grs.	2·3 grs. sugar.		

From these experiments on healthy urine it follows:—

1. That by the alcoholic process, when 140 c. c. to 3,000 c. c. of urine were employed, no result was obtained by the reduction test, by Pettenkofer's test, or by the saccharimeter, chiefly because the percentage of alcohol was not great enough.

2. That by the lead process, most conclusive results were obtained, qualitatively and quantitatively, by the reduction test, by fermentation, and by the saccharimeter.

By the reduction test, qualitatively, 200 c. c. of urine gave no evidence; 500 c. c. failed, and 500 c. c. gave proof of sugar; 1,000 c. c. gave very evident sugar; 3,000 c. c. gave much more proof. By this test, quantitatively 1,000 c. c. of one man gave 2·2, 1·5, 1·4, and 1·8 grs. of sugar. The same quantity of urine in another man gave 3·0 and 2·3 grs. of sugar in one litre.

By the saccharimeter, quantitatively, 5,000 c. c. of urine, partly used, gave 2°, 3°, and 4° of rotation. In another man, 5° were observed. In a third man, a smaller quantity of urine gave 1° to 2° of rotation.

By this test quantitatively, 5,000 c. c. of one man, all used, gave 7° to 8° of rotation. The same quantity from another man, gave 10° to 11°.

By fermentation, qualitatively, an unknown quantity fermented, gave distinct evidence of alcohol and 2·1 grs. of carbonic acid.

Quantitatively, 10,000 c. c. of urine were used, and ultimately, 1·64 gr. of carbonic acid was obtained.

14,000 c. c. of the same urine gave most positive proof of alcohol and 1·8 gr. of carbonic acid.

These experiments, therefore, fully confirm Professor Brücke's statement, that sugar exists in healthy urine. By obtaining alcohol from the fermented fluid, and by never failing to find rotation when the saccharimeter was used, provided sufficient urine had been taken for the experiments, I have added to the evidence given in his original paper.

III.—*Analysis of the Saline Water of Purton, near Swindon, North Wilts.*

By Henry M. Noad, Ph.D., F.R.S., and C.S.

The water rises in a field on the Oxford Clay, which reaches from the bottom of the hill on which the village of Purton is built, to the river Thames at Cricklade, a distance of about three miles, the spring being about midway between both. The soil of Purton rests on the limestone. The field in which the spring rises has long been known in the neighbourhood as "Salt's Hole." The medicinal properties of the water are held in high esteem by the inhabitants of Purton, and the proprietor has recently erected a pump-room round the well, from which about 120 gallons of the water can be pumped up daily.

The water, which was analysed at the request of Dr. Kinneir, of Purton, was collected by myself in the month of January in the present year. As pumped up from the well, it was quite clear, and remained so after long standing. While the pump was in action, a faint but decided smell of sulphuretted hydrogen was perceptible, but the water itself, while still, had no such odour.

The temperature of the water was nearly the same as that of the air. Specific gravity, at 60°F., = 1·0056. Free carbonic acid, 50 cubic inches per imperial gallon, the water being slowly pumped up from the well.

The analysis was performed in the usual manner, the iodine, which could be distinctly recognised in one pint of the water, being estimated as *protiodide of palladium*.

In the arrangement of the results of analysis, the strongest acid is assumed to be combined with the strongest base; and the lime and magnesia thrown down as carbonates by boiling, are considered as existing in the water as carbonates held in solution by carbonic acid.

Direct results of analysis calculated to 1 imperial pint.

Bases.

Experiment.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.....	6·422	4·748	18·90	1·179	17·721
II.....	6·257	4·783	19·33	1·020	18·310
Mean	6·340	4·765	19·10	1·099	18·016

Acids

(*or elements replacing them*).

Experiment.	Sulphuric Acid.	Chlorine.	Iodine with traces of Bromine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid as Carbonate of Lime and Carbonate of Magnesia.	Carbonic Acid, free.	Phosphoric Acid.	Apocrenic Acid.
I....	24·00	2·82	„	0·27	„	2·38	„	„	„
II....	23·80	2·80	„	0·29	„	2·36	„	„	„
Mean	23·90	2·81	0·0094	0·28	5·403	2·37	3·133	0·031	0·112

Verification for Lime.

Experiment.	Lime precipitated by boiling.	Lime left in solution after boiling.	Total by Calculation.	Total by Experiment.
I.	2·828	3·280	6·108	6·422
II.	2·857	3·310	6·077	6·257
Mean	2·842	3·296	6·092	6·340

Verification for Magnesia.

Experiment.	Magnesia precipitated by boiling.	Magnesia left in solution.	Total by Calculation.	Total by Experiment.
I	0·11	4·735	4·845	4·748
II	0·15	4·785	4·945	4·783
Mean	0·13	4·755	4·890	4·765

RESIDUE LEFT ON EVAPORATION.

Experiment.	Mineral Residue.	Organic Residue.	Total Residue.
I	51·02	0·114	51·114
II	51·21	0·110	51·320
Mean	51·11	0·112	51·217

Solid Contents of an imperial pint as determined by analysis.

Carbonate of lime	5·0760
Carbonate of magnesia	0·2630
Lime (not as carbonate)	3·2200
Magnesia (not as carbonate)	4·7580
Potash	0·6930
Soda	9·5460
Chlorine	2·8100
Sulphuric acid	23·9000
Silica	0·2800
Phosphoric acid	0·0310
Bromine	traces
Iodine	0·0094
Crenic acid	traces
Apocrenic acid	0·1120
	50·6984
Residue left on Evaporation	51·2170

Saline Constituents in one Imperial Gallon.

Carbonate of lime	40·608
Carbonate of magnesia	2·104
Sulphate of potash	10·264
Sulphate of soda	174·904
Sulphate of lime	62·560
Sulphate of magnesia	76·592
Chloride of magnesium	30·000

Iodide of sodium	0·088
Silica	2·080
Phosphoric acid	0·248
Crenic acid	traces
Apocrenic acid	0·896
Bromine	traces
	400·344

IV.—*On the Composition of Purton Saline Water.*

By Augustus Voelcker, Ph. D.

(professor of chemistry in the royal agricultural college, cirencester.)

Noticing that Dr. Noad intends reading on the 17th December, 1860, a paper on the analysis of Purton saline water, I beg likewise to communicate an analysis of that water, which I made for the proprietor in October, 1859.

The following are the direct results of the analysis. An imperial gallon contains:—

	Grains.
Organic matter and water of combination (being loss obtained on heating residue, dried at 320°F)	8·750
Lime	34·536
Magnesia	25·736
Oxides of iron and alumina, with traces of phosporic acid	·280
Potash	20·707
Soda	49·006
Chloride of sodium	34·297
Sulphuric acid	165·074
Soluble silica	1·280
Iodine	0·056
Bromine	·080
Carbonic acid	33·090
Sulphuretted hydrogen	traces
Specific gravity of water	1·0045

These constituents arranged into compounds give the following results :—

	Grains per imp. gal.
Organic matter and water of combination (loss on drying residue at 320°F)	8·750
Sulphate of soda	112·239
Sulphate of magnesia	77·208
Bromide of magnesium	·092
Iodide of sodium	·066
Chloride of sodium	34·297
Sulphate of lime	83·873
Sulphate of potash	1·916
Carbonate of potash	28·880
Oxides of iron and alumina with traces of phosphoric acid	·280
Silica	1·280
Solid residue, dried at 320°F per imperial gallon	348·881
Free carbonic acid	23·820

Dr. Noad has communicated his results to me. They differ materially from mine. But the fact that the water analysed by Dr. Noad contains a great deal more solid matter than the water analysed by me, shows sufficiently that we examined two different specimens of Purton water. I have determined at various times the amount of residue which is left on evaporation, and find great differences in the total amount of total saline matters. Probably the composition of the saline residue varies at different seasons, and the water, like other saline waters obtained only in limited quantities, is not always of the same composition.

With respect to the arrangement of the direct results of the analysis into compounds, I beg to observe that I have purposely united carbonic acid with potash and not with lime. In his arrangement of results, Dr. Noad does not give any alkaline carbonates. The Purton water, which I examined, however, contains alkaline carbonates, for it exhibits a strong alkaline reaction to litmus paper, even before evaporation.

It is of course impossible to say what proportions of the carbonic acid and sulphuric acid are united with lime and the alkalies, and I have deviated from the ordinary mode of uniting acids and bases together, because the Purton water in its natural condition really contains alkaline carbonates.

V.— *On the Basic Carbonates of Copper, with some Remarks upon the Carbonates of Nickel and Cobalt.*

By Frederick Field.

In a paper upon this subject, lately published in the "Chemical News," and in Abstract at page 70 of this volume, the singular effect of a strong solution of carbonate of soda upon malachite was mentioned, together with the action of boiling water upon the same mineral. In both instances it speedily becomes black, being converted into the black oxide, with brisk evolution of carbonic acid. When the blue carbonate of copper (azurite) $3CuO.2CO_2.HO$ is subjected to similar treatment, exactly the same phenomenon occurs, the whole of the carbonic acid being expelled, the action of pure water facilitating the decomposition far more readily than the solution of carbonate of soda. In a memoir upon the carbonates of copper, Rose* informs us, that the green carbonate formed on adding a salt of copper to carbonate of soda, is converted into the oxide by long digestion with boiling water, but no blue compound is obtained. Artificial malachite may, however, be formed from azurite, by heating the latter for some little time in a rather concentrated solution of bicarbonate of soda. A bright blue liquid is produced, which, after lengthened ebullition, deposits a green powder, containing exactly the amount of oxide of copper which is found in malachite; it is this precipitate, which has a similar composition to that which is produced by boiling a solution of malachite in carbonate of soda, does not part with its water under a temperature of 380° F, and is evidently formed by the elimination of 1 atom of carbonic acid from 2 atoms of azurite, one atom of water at the same time taking the place of the carbonic acid—

$$2\,(3CuO.\,2CO_2.\,HO) - CO_2 + HO = 3\,(2CuO.\,CO_2.\,HO)$$

Deville† mentions that when a salt of copper is gradually added to a strong solution of carbonate of soda, nearly the whole of the alkali is precipitated with the copper, in brilliant crystals of the double carbonate. In all my experiments, warm solutions were employed, in which case no double compound was formed, but a highly basic carbonate, and subsequently black oxide, were alone produced.

* Pogg. Ann. lxxxiv, 461; Ann. Ch. Pharm. lxxx, 236.
† Ann. Ch. Phys. [3], xxxiii, 75

Carbonate of Cobalt. The various carbonates of cobalt have been intimately studied by Rose,* who remarks that the composition of these compounds depends very much upon the concentration of the solutions, and upon the temperature employed during the precipitation. When sulphate of cobalt is mixed with carbonate of soda, a precipitate is formed having the formula $2(CoO.\ CO_2)+3(CoO.\ HO)+Aq.$, either from concentrated or from weak solutions, and it is only when dilute solutions are decomposed at the boiling point, that a precipitate is obtained which approximates to $CoO.\ CO_2+2(CoO.\ HO), Aq.$ The same chemist further informs us, that when sulphate of cobalt is treated with an excess of bicarbonate of potash in the cold, there is formed, with brisk evolution of carbonic acid, a voluminous precipitate, which by long standing is transformed into a mass of tolerably distinct crystals, having for their composition $KO.\ CO_2+CoO.\ CO_2+9HO$. The rather curious phenomena exhibited by the addition of dilute copper-salts to a strong solution of carbonate of soda, the latter in great excess, led me to investigate the reaction induced upon the salts of cobalt under similar circumstances. When dilute nitrate of cobalt is added to bicarbonate of soda, no precipitate occurs, until a considerable quantity has been introduced. The solution has a beautiful violet colour, and can be brought to ebullition, and even maintained at a boiling temperature for some time without undergoing complete decomposition. The precipitate which forms after a further addition of the cobalt-salt, has a pure pink colour, which scarcely changes its tint, even when the liquid in which it is suspended is boiled for several hours. This compound appears to hold carbonate soda with remarkable tenacity; indeed it seems impossible to free it from the latter by any amount of ordinary washing. When the filtrate no longer shows signs of alkalinity to test-paper, the precipitate removed from the filter and heated with a fresh portion of distilled water, still yields an alkaline solution. On filtering off the carbonate of soda, and heating with water as just described, the pink colour quickly vanishes, and it becomes brown. When nitrate of cobalt is added to an excess of carbonate of soda, carefully freed from all excess of carbonic acid, the precipitate is not pink but blue, maintains its colour with some persistency as long as the supernatant liquid is strongly alkaline, and is quite as difficult to free

* Pogg. Ann. lxxxiv. 548. Ann. Ch. Pharm. lxxx. 237.

from adhering soda as the other compound. Cobalt, it appears, differs somewhat from copper when acted upon by either the carbonate or the bicarbonate of soda. When a salt of copper, it may be remembered, is added to a strong hot solution of the former, immediate decomposition takes place, carbonic acid is evolved, and a highly basic carbonate formed, which is ultimately converted into the black oxide. When the bicarbonate is employed, a green precipitate of hydrated bicarbonate is obtained. In order to see if oxide of cobalt altogether free from carbonic acid can be procured by long-continued boiling in distilled water, solutions of the nitrate of that metal and carbonate of soda were mixed, neither being in great excess. The peach-coloured compound was well washed and suspended in a pint of water, which was brought to ebullition and maintained at that temperature for about ten hours, water being added from time to time to compensate for the loss resulting from evaporation. The precipitate soon changed colour, becoming brown, and ultimately black. After filtration, it was dried at 212° Fah. and analysed, yielding 12·34 of carbonic acid, and 78·51 black oxide of cobalt (Co_3O_4) upon intense ignition. The carbonate of cobalt, as it originally existed, was composed of 2(CoO. CO_2) 3(CoO. HO) + Aq., and by the action of water at 212°, parted with a portion of its carbonic acid, and became partially converted into the sesquioxide. A compound containing 12·21 carbonic acid, which upon ignition would yield 78·41 of the protoperoxide of cobalt, would have the following formula :—

$$2\,(CoO.\,CO_2)\;3\,(CoO.\,HO) + Aq + Co_2O_3,\,HO.$$

Found.	Calculated.
$CO_2 = 12{\cdot}34$	CO_2 12·12
Co_3O_4 78·51	$Co_3\,O_4$ 78·41.

That this compound is a mixture of ordinary carbonate of cobalt with the hydrated sesquioxide, arises from the action of dilute hydrochloric acid. When this acid, diluted with three or four times its bulk of water, is added to the carbonate, the latter is almost instantaneously dissolved, with brisk disengagement of carbonic acid. Upon the sesquioxide, however, it produces little effect. When cold and comparatively weak, the liquid becomes only slightly tinged, after being in contact with it many hours. Exactly the same phenomena occur in the compound just mentioned. On the addition of dilute hydrochloric acid, the whole of the

carbonate is immediately dissolved, a black powder remaining untouched. When warm and concentrated acid is added to this, it is gradually decomposed, solution is effected, and chlorine is evolved. When nitrate of cobalt is added to a solution of bicarbonate of soda containing a small quantity of the hypochlorite of that alkali, an intense and beautiful green colour is produced, and no elimination of carbonic acid results. So strong is the colouring power of this body, that 0·2 of a grain of nitrate of cobalt will colour eight ounces of solution, a clear bright green, as dark as a tolerably concentrated solution of chloride of copper. Large quantities of oxide of cobalt can be dissolved in this way, and the liquid, if not too strong, may be boiled for some time without undergoing decomposition. When, however, the nitrate of cobalt is rather concentrated, and heat is applied, a brisk evolution of carbonic acid takes place, and sesquioxide is precipitated, which, adhering in a scaly mass to the sides of the glass, and being removed by agitation, floats about the liquid in brilliant iridescent plates, appearing at first sight to be beautifully and highly crystalline.

Cobalt cannot be separated from iron or manganese by this method, although every degree of concentration and temperature has been tried. When the solution is not sufficiently warm, a small quantity of iron is dissolved, when, on the other hand, considerable heat is applied, a small quantity of cobalt remains with the precipitate.

Carbonates of Nickel. Nickel-salts exhibit, generally speaking, the same reactions as those of cobalt in excess of carbonate of soda. I have tried in vain to procure oxide of nickel perfectly free from carbonic acid by boiling the carbonate in water, although the resulting compound was very highly basic. No peroxide however is formed, as in the case of cobalt. The carbonates of nickel, when precipitated in very strong solutions of the alkaline carbonates, appear to hold the latter with as great tenacity as the cobalt-compound.

VI. — *Preliminary Note concerning a new Homologue of Benzoic Acid.*

By Arthur H. Church, B.A.

Attempts have been made to effect the oxidation of benzol by means of an oxidizing mixture consisting of bichromate of potassium and sulphuric acid; it has been found, however, that the hydrocarbon remained unattacked. Not so, however, with the other members of the same series, toluol and cumol yielding benzoic acid, and cymol, an acid of totally different properties and constitution. I have succeeded in producing from benzol an apparently new oxygenated body, presenting all the properties one might expect to find in a homologue of benzoic acid containing CH_2 less than that substance. This supposition is strengthened by the result of an experiment in which nitrobenzol was made to yield an acid body apparently standing in the same relation to the first-mentioned new acid as nitrobenzol to benzol.

The following was the plan pursued in the preparation of the new acids: Pure benzol was dissolved in a slight excess of Nordhausen sulphuric acid, and the mixture heated for some time to 100° C. It was then diluted with about its bulk of water, and transferred to a retort. Small fragments of bichromate of potassium were added gradually to the liquid, the temperature of which was slowly raised. The acid was found partly floating on, and partly dissolved in, the aqueous distillate. Great care must be taken lest the oxidation proceed too actively, and the product be lost. The acid is a white fusible and crystalline solid, distinguished from Collinic acid, to which the same formula has been assigned, by its far greater solubility in hot water. The analytical results indicate the formula—

$C_6H_4O_2$* for the acid; and
$C_6H_3MO_2$ for the salts.

The fact that benzol is reproduced in large quantity from sulphobenzolate of ammonium $C_6H_5.NH_4.SO_3$, when that salt is submitted to dry distillation, suggested the probability that the

* C = 12; O = 16; S = 32; H = 1.

acid itself, when acted on by an oxidizing agent, might yield the products which we should expect to obtain by the oxidation of the original benzol.

When sulphotoluolic and sulphocumolic acids are similarly treated, benzoic acid is the corresponding product: with sulphocymolic acid, a white powder, apparently identical with the insolinic acid of Hofmann, is obtained.

Nitrobenzol is attacked with the utmost difficulty by the chromic acid mixture. By long boiling it is, however, at length converted into a white acid, which crystallizes from boiling water in large nacreous plates. Analysis has led to the formula—

$$C_6H_3(NO_2)O_2 \text{ for the acid ; and}$$
$$C_6H_2(NO_2)MO_2 \text{ for the salts.}$$

Nitrotoluol and nitrocumol are oxidized with considerable ease under similar conditions, yielding nitrobenzoic acid in abundance. This is the case also with nitrosulphotoluolic acid, $C_7H_6NO_2$. H. SO_3, the acid sulphite of nitrotoluenyl.

The acid from nitrobenzol was obtained in June last, but MM. Cloëz and Mignet announce in the "Comptes Rendus" of January 21st, 1861, that they have obtained a new acid from nitrobenzol by oxidizing it with permanganate of potassium or with a mixture of bichromate of potassium and nitric acid. To their acid they assign the expression—

$$C_9H_7(NO_2)O_3,$$

But it is not easy to see how such a body can be derived from the oxidation of nitrobenzol, which contains only C_6. Indeed the authors are by no means certain of the purity of the nitrobenzol which they employed, and they even go so far as to suggest that the acid which they describe may have owed its origin to some foreign body with which the commercial nitrobenzol on which they operated may have been contaminated.

VII.—*On some products of the Action of Dilute Nitric Acid on some Hydrocarbons of the Benzol Series.*

(PRELIMINARY NOTICE.)

By Warren DeLaRue, Ph. D., F.R.S., etc. and Hugo Müller, Ph. D., F.C.S.

Some years ago, whilst investigating the nature of Burmese naphtha, and examining the products of the action of nitric acid on the hydrocarbons obtained therefrom, our attention was directed to similar experiments made many years ago by Laurent, who discovered, amongst the products of the action of nitric acid on coal-tar naphtha and the naphtha obtained by distilling bituminous schist, a new acid called *ampelic acid*, of the interesting composition $C_7H_6O_3$,* being isomeric with salicylic acid. As we failed to find ampelic acid amongst the products resulting from the action of nitric acid on Burmese naphtha, we repeated Laurent's experiments with coal-tar naphtha, but with no better result; we could detect no substance corresponding with his description of ampelic acid. These experiments with coal-tar naphtha, in consequence of their giving a negative result with regard to ampelic acid, occupied our attention for some time, as we were desirous of making out the somewhat complex nature of the products resulting from the long-continued action of nitric acid on this particular class of hydrocarbons. The coal-tar naphtha used consisted principally of toluol, xylol, and pseudocumol.

Reserving for a further communication the details of our investigation, we will simply state at present that we finally succeeded in obtaining four different acids of the aromatic series. The interest attaching to some of them may justify the bringing of our results in an incomplete form under the notice of the Society, and we are the more induced to take this step, because we believe that other chemists are directing their attention to similar products. The preparation and separation of the substances under consideration is attended with the expenditure of a

* Carbon = 12; Oxygen = 16; Hydrogen = 1.

considerable time, and the completion of our researches may consequently be somewhat delayed.

For our experiments we distilled in a capacious retort, purified coal-tar naphtha with about 15 times its volume of dilute nitric acid (containing 1 volume of commercial acid to 3 volumes of water). The action of the acid is very slow; but after several days, the hydrocarbons are changed into a heavy liquid which gradually becomes converted into a yellowish-white flocculent substance, partly suspended in the acid and partly dissolved in it. When no further change is perceptible, the retort is allowed to cool. The resulting yellowish-white substance is separated by filtration from the acid mother-liquor, and treated with a large quantity of boiling water, which dissolves the greater part, and leaves some semi-liquid nitro-compounds, and a few other substances undissolved. On cooling, the aqueous solution deposits the white substance it had held in solution. For the purpose of separating the adhering nitro-compounds and nitro-acids, the white substance is dissolved in ammonia, mixed with sulphide of ammonium, and boiled until the nitro-compounds are converted into amidogen-compounds. To the resulting deep-red solution are then added a few drops of hydrochloric acid, which causes a brown precipitate of the amidogen-compounds, separable by filtration. The filtrate is then completely precipitated by a further addition of hydrochloric acid, and the precipitate, consisting of several acids, is then filtered off and treated again with a large quantity of boiling water, which leaves undissolved an insoluble acid. The substance deposited on cooling is filtered off and dried. After having been previously fused, it is introduced into a small retort and then submitted to careful distillation. At first there distils over a colourless liquid, which very soon solidifies, like palmitic acid, in the neck of the retort. After a certain time, a new substance makes its appearance and crystallizes in large acicular crystals in the bulb of the retort, just above the boiling liquid. The distillation is stopped at this point; and after cooling, the first-named substance in the neck of the retort is removed by gently warming it. On subsequently continuing the distillation, very little passes into the neck of the retort, the residue becoming gradually black and solid, whilst the upper part of the bulb becomes filled with magnificent crystals. When the formation of the latter ceases, the operation is discontinued. The palmitic-acid-like distillate is a mixture of two acids, and for the

purpose of separating them, it is powdered and brought into contact with purified Burmese naphtha boiling at about 90° C. (probably hydruret of capryl C_8H_{18}). The hydrocarbon extracts one part of the distillate, leaving the other undissolved. After the hydrocarbon has been filtered, it is distilled, whereon a liquid residue remains in the retort, and gradually solidifies to a beautiful crystalline mass. This crystalline substance is an acid possessing the general properties of benzoic acid. A combustion made with material not quite free from the second acid (which we succeeded at last in separating completely with Burmese naptha, which we had not employed in our first experiment), gave numbers ($C_6H_4O_2$), approaching very nearly those of the next lower homologue of benzoic acid. This new acid fuses at about 60° C., but occasionally remains liquid, even at the ordinary temperature, especially when not quite pure. It is heavier than water, and mixes in all proportions with alcohol; it is only slightly soluble in cold water, but more so in boiling water. From a saturated hot solution it separates, whilst the solution is cooling, as a heavy oil which sometimes solidifies immediately, but at other times only after a certain interval. This acid is slightly volatile, even at ordinary temperatures, for it covers itself with beautiful crystallizations. It possesses a very acrid taste. When boiled with water, it volatilizes to a considerable extent. It can be distilled *per se* without decomposition, and forms well-crystallized salts with the alkalies. From this description it will be perceived that this acid bears a great similarity to an acid which was described only a few months since by Fröhde, who obtained it, in small quantities amongst the products of oxidation of glue and albuminous substances, and called it accordingly *Collidinic acid*. The difference which still exists may be cleared up by further investigation; for Fröhde had not material enough for combustion, nor was his acid quite free from benzoic acid. Although the quantity of this acid formed from the hydrocarbons is not great, we have no doubt that this source will furnish the material for a complete investigation of this highly interesting acid.

The acid which is left undissolved by the Burmese naphtha (hydruret of capryl) has the composition of benzoic acid, but it differs in some points from the true benzoic acid, wanting its great power of crystallization. It seems not unlikely that this acid is identical with *salylic acid* the isomer of benzoic acid quite recently described by Kolbe and Lautemann ($C_7H_6O_2$).

The before-named crystalline sublimate which deposits in the bulb of the retort is an acid which differs considerably from any of the known acids. In its chemical properties it resembles closely terephthalic acid, but it differs from this acid in its capability of forming large and distinct crystals when it is sublimed. The crystals when obtained by sublimation form arborescent masses of large prismatic crystals. The quantity of the acid obtained was too small to ascertain its chemical nature more fully.

Lastly, the insoluble acid, which remains undissolved when the precipitate is obtained by the addition of hydrochloric acid to the ammoniacal solution of the crude acids, after treatment by sulphide of ammonium, is principally *terephthalic acid* ($C_8H_6O_4$).

The terephthalic acid is dried and converted into terephthalic chloride, which, when heated with methylic alcohol, furnishes terephthalate of methyl, which can be readily purified by re-crystallization from alcohol, and thus when decomposed offers a ready means of procuring terephthalic acid in a pure state.

VIII.—*On the Bisulphide of Iodine.*

By Frederick Guthrie.

An examination of the action of certain compound halogens on some of the olefines, has led me to consider incidentally the preparation of some of the compound halogens in the pure state.

Of compound halogens, while the constitution of none is more invariable and definite than that of the bisulphide of chlorine,—the bisulphide of iodine can scarcely be said to have been prepared, notwithstanding the strong analogy between chlorine and iodine.

That iodine combines with sulphur is well known; that such combination is attended by the liberation of heat is equally well established; and since homogeneous mixtures of the two may be prepared in all proportions, it is clear that a substance having the percentage composition of the bisulphide of iodine may be formed. Bodies so formed have little or no title to the name of chemical compounds.

If we remember, on the one hand, the fact which I have abun-

dantly proved on former occasions, that an equivalent of bisulphide of chlorine functions as two equivalents of chlorine, or, as some chemists would express it, that the molecule of bisulphide of chlorine is biatomic; and if we further remember that at least two equivalents of chlorine or of zinc are required to *recompose* iodide of ethyl, according to the equations—

$$(1)^* \quad C_4H_5I + 2Cl = C_4H_5Cl + ICl$$
$$(2) \quad C_4H_5I + 2Zn = C_4H_5Zn + ZnI$$

we must be prepared to anticipate the analogous re-action—

$$(3) \quad C_4H_5I + S_2Cl = C_4H_5Cl + S_2I:$$

This the more, because in the case of certain compounds, such as NaSn, we find—

$$(4) \quad C_4H_5I + NaSn = C_4H_5Sn + NaI.$$

The method I employ for the preparation of the bisulphide of iodine is in fact based upon the validity of equation (3).

Recompositions quite akin to (3) are suffered by the iodides of methyl and of amyl; whence we may assert the general equation—

$$(5) \quad C_nH_{n+1}I + S_2Cl = C_nH_{n+1}Cl + 3_2I.$$

For obvious reasons the ethyl-compound is preferred.

The reciprocal action of iodide of ethyl and bisulphide of chlorine is perhaps as interesting in its manner as in its result. The two liquids may be mixed in all proportions without a greater change in colour than is due to the dilution of the coloured sulphide by the colourless iodide; neither is heat liberated nor other immediate token given of chemical change taking place. The change appears to be complete in about twelve hours. If the vessel be open to the air, the chloride of ethyl evaporates as it is formed, leaving the bisulphide of iodine in magnificent crystals, contaminated, however, by the products of the action of the moisture of the air upon the bisulphide of chlorine. For this reason the process is best conducted in a hermetically sealed tube. The co-reagents are used in the proportions shown by the equation—a very slight excess of the iodide being added.

* Equation (1) expresses only the initial recomposition—the ultimate products are HCl,ICl_3 and chlorine substitution-products of C_4H_5Cl.

On opening a tube so charged, which has been left over night, and applying the heat of the hand, the chloride of ethyl escapes. A gentle heat suffices to expel the residual iodide of ethyl—whereupon the bisulphide of iodine is left in the form of fine tabular crystals of the lustre of iodine and in a state of absolute purity.

Although the exact composition of the substance may be fairly deduced from its synthesis, it was submitted to analysis in the following way.

0·3270 grm. was heated in a combustion-tube with nitrate of potash and carbonate of soda, whereby the iodine and sulphur were converted respectively into iodide and sulphate of potassium. They were then estimated in the usual way:

	Calculated.	Found.
S_2	20·13	20·28
I	79·87	79·81
	100·00	100·09

Though in this note, this curious re-action is considered as a means of preparing the compound halogen S_2I, it is perhaps of equal interest as offering a method for preparing an organic chloride from its iodide ;—a problem hitherto difficult and cumbrous in solution, albeit its inverse is often easy and of frequent occurrence.

On Azobenzol and Benzidine.

By P. W. Hofmann.

[From the Proceedings of the Royal Society for June, 1860.]

Among the numerous compounds into which benzol, when submitted to reagents, is converted, *azobenzol* and its derivatives have as yet received but limited attention. Although more than twenty-five years have elapsed since this interesting body was discovered by Mitscherlich, both its formation and its constitution remain still doubtful.

Mitscherlich*, who discovered azobenzol in 1834, when submitting nitrobenzol to the action of an alcoholic solution of potassa, represented this compound by the formula

$$C_6H_5N\dagger,$$

but left the reaction which gives rise to the formation of azobenzol unexplained. In 1845 this body was reprepared by Hofmann and Muspratt‡, who observed among the collateral products of the reaction *aniline* and *oxalic acid*. They represent the formation of azobenzol by the equation

$$\underset{\text{Nitrobenzol.}}{2C_6H_5NO_2} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Azobenzol.}}{C_6H_5N} + \underset{\text{Phenylamine.}}{C_6H_7N} + \underset{\text{Oxalic acid.}}{C_2H_2O_4} + H_2O,$$

adding at the same time that they are far from considering this equation as more than the representation of *one* phase of the transformation of nitrobenzol, since several other rather indefinite compounds are formed simultaneously.

At about the same period Zinin made the interesting observation that azobenzol is capable of fixing hydrogen and of being thereby converted into a well-defined base, benzidine, which he represented by the formula

$$C_6H_6N.$$

Considering the physical characters both of azobenzol and of benzidine, especially the high boiling-points of these substances, and the ratio of hydrogen and nitrogen in the latter compound,

* Pogg. Ann, xxxii. p. 224.
† H=1, O=16, C=12, &c.
‡ Mem. of the Chem. Soc. vol. iii. p. 113.

the sum of the number of equivalents of these two elements not being divisible by 2, many chemists were inclined to double the formulæ of both bodies, and to represent them by the following expressions:—

Azobenzol ..... $C_{12}H_{10}N_2$
Benzidine ..... $C_{12}H_{12}N_2$

This view received the first experimental confirmation in the formation of the nitro-derivatives of azobenzol, which were examined in 1849 by Gerhardt and Laurent. The formation of

Nitrazobenzol.... $C_{12}H_9N_3O_2 = C_{12}[H_9(NO_2)]\ N_2$,
Dinitrazobenzol.. $C_{12}H_8N_4O_4 = C_{12}[H_8(NO_2)_2]N_2$,

and of several derivatives of these bodies, having established the C_{12}-formula of azobenzol, but little doubt could be entertained regarding the formula of benzidine, which is as readily obtained from azobenzol by reducing agents, as it may be reconverted into azobenzol by nitric acid*.

The molecular value of benzidine being thus almost exclusively fixed by the determination of the formula of the compound from which it originates, it was of some interest to obtain additional experimental evidence for the molecular weight of azobenzol.

With this view I have determined the vapour-density of azobenzol. This body boiling at a rather high temperature, I have availed myself of the method of displacement lately proposed by Professor Hofmann. Experiment proved the density of the azobenzol-vapour to be 94 referred to hydrogen as unity, or 6·50 referred to air. The theoretical vapour-density of azobenzol, assuming that one molecule of this compound furnishes, like the rest of well-examined substances, 2 vols. of vapour†, is $\frac{182}{2}=91$ referred to hydrogen, and 6·32 referred to air.

This determination of the vapour-density, then, plainly confirms the higher molecular weights proposed for azobenzol and for benzidine.

When determining the vapour-density of azobenzol, I had occasion to observe that, probably in consequence of a typographical error, the boiling-point of this compound is misstated in all the manuals which I could consult, and even in the original memoirs of Mitscherlich himself. The boiling-point is stated to be 193° C., whilst it is in reality 293° C.

Benzidine, when expressed by the formula

$$C_{12}H_{12}N_2,$$

presents itself as a well-defined diacid diamine. The molecular construction of the diatomic base remained to be decided.

* Noble, Journal of the Chem. Soc. vol. viii. p. 293. †$H_2O = 2$ vols.

I have endeavoured to solve this problem by the process of ethylation, as yet the simplest and the best guide in determining questions of this kind. Benzidine in the presence of alcohol is rapidly attacked by iodide of ethyl. After two hours' digestion at 100° C. in sealed tubes, the reaction is complete. The solution on evaporation yields a crystalline iodide,

$$C_{16}H_{22}N_2I_2=C_{12}H_{12}(C_2H_5)_2N_2I_2,$$

from which ammonia separates a solid crystalline base very similar to benzidine. This compound, which fuses at 65° C., and resolidifies at 60° C., is *diethylbenzidine:*

$$C_{16}H_{20}N_2=C_{12}H_{10}(C_2H_5)_2N_2,$$

which forms well-crystallizable salts with the acids, and yields with dichloride of platinum a difficulty soluble crystalline platinum-salt containing

$$C_{16}H_{22}N_2Cl_2,2PtCl_2.$$

When diethylbenzidine is treated again with iodide of ethyl, the phenomena previously observed are repeated. The iodide

$$C_{20}H_{30}N_2I_2=C_{12}H_{10}(C_2H_5)_4N_2I_2$$

is formed, which when decomposed by ammonia yields *tetrethylbenzidine*

$$C_{20}H_{28}N_2=C_{12}H_8(C_2H_5)_4N_2.$$

Tetrethylbenzidine resembles the diethylated and the non-ethylated base. It fuses at 85° C., resolidifying at 80° C., produces with the acids crystalline compounds, and furnishes with dichloride of platinum, a platinum-salt of the formula

$$C_{20}H_{30}N_2Cl_2,2PtCl_2.$$

The further action of iodide of ethyl upon tetrethylbenzidine is extremely slow. After 12 hours' digestion at 100° C. only a very minute quantity of the base had been transformed into an iodide. Iodide of methyl, on the other hand, acts with great energy. An hour's digestion is sufficient to produce the final diammonium-compound.

The iodide

$$C_{22}H_{34}N_2I_2=C_{12}H_8(C_2H_5)_4(CH_3)_2N_2I_2$$

is very difficultly soluble in absolute alcohol, but dissolves with facility in boiling water, from which it is deposited on cooling, in long beautiful needles. The solution of this iodide is no longer precipitated by ammonia, but yields with oxide of silver a powerfully alkaline solution, exhibiting all the characters of the completely substituted ammonium- and diammonium-bases discovered by Professor Hofmann. The solution of this dimethyl-tetrethylated base, which contains

$$C_{22}H_{36}N_2O_2=\left.\begin{matrix}C_{12}H_8(C_2H_5)_4(CH_3)_2N_2\\H_2\end{matrix}\right\}O_2,$$

is not further acted upon by either iodide of ethyl or methyl. With acids it forms a series of salts which are remarkable for the beauty with which they crystallize. The platinum-salt is almost insoluble in water, but soluble with difficulty in concentrated boiling hydrochloric acid, crystallizing from this solution on cooling in beautiful needles. This salt contains

$$C_{22}H_{34}N_2Cl_2, 2PtCl_2.$$

The above experiments appear to establish the molecular construction of benzidine in a satisfactory manner. This base is obviously a primary diamine, in which the molecular group $C_{12}H_8$, whatever its nature may be, functions as a diatomic radical. A glance at the subjoined Table exhibits the construction of benzidine and of the several compounds which I have described.

Diamines.

Benzidine.....	$(C_{12}H_8)''$ H_2 H_2	N_2,
Diethylated benzidine	$(C_{12}H_8)''$ $(C_2H_5)_2$ $(H_2)_2$	N_2,
Tetrethylated benzidine....	$(C_{12}H_8)''$ $(C_2H_5)_2$ $(C_2H_5)_2$	N_2.

Iodides of Diammoniums.

Primary.....	$[(C_{12}H_8)''$	H_6		$N_2]''I_2$,
Secondary ..	$[(C_{12}H_8)''$	H_4	$(C_2H_5)_2N_2]''I_2$,	
Tertiary.....	$[(C_{12}H_8)''$	H_2	$(C_2H_5)_4N_2]''I_2$,	
Quartary.....	$[(C_{12}H_8)''$	$(CH_3)_2$	$(C_2H_5)_4N_2]''I_2$.	

The experiments described in this note were performed in Professor Hofmann's laboratory.

On the Constitution of Oil of Cajeput.

By Maximilian Schmidl.

(From the Transactions of the Royal Society of Edinburgh, Vol. XXII., Part VI., p. 360.)

Oil of Cajeput is prepared in the East Indies, by distilling the leaves of *Melaleuca Leucodendron* with water. It was formerly used to a great extent as an external and even as an internal medicine; but has now become more or less obsolete, and is seldom

met with in a pure or unchanged state, except in the hands of wholesale druggists. As introduced into Europe, it possesses a light green colour, resembling that of a dilute solution of chloride of chromium, which is caused by a resinous colouring matter dissolved in it in very small quantity.

The colour of the crude oil is also partly due to copper, the presence of which may be accounted for, either by the use of a copper head in the distilling apparatus of the Indians, or by intentional adulteration resorted to for preserving the green colour of the oil, which otherwise changes gradually by oxidation to a reddish-brown, the oil then becoming unsaleable for medicinal purposes. That the oil possesses a green colour of its own, is proved by the fact that the colour remains after the complete removal of the copper by sulphuretted hydrogen.

Oil of cajeput consists mainly of the bihydrate of a hydrocarbon (*cajputene*) isomeric with oil of turpentine. Its specific gravity is 0·926 at 10° C. On submitting it to fractional distillation, bihydrate of cajputene, which constitutes about two-thirds of the crude oil, passes over between 175° and 178° C.; smaller fractions, perhaps products of decomposition, are obtained from 178° to 240° C., and from 240° to 250°, and at 250° only a small residue is left, consisting of carbonaceous and resinous matter mixed with metallic copper. On treating this residue with ether, a green solution is obtained, which, when evaporated, leaves a green resin, soluble in the portion which boils between 175° and 178° C., and capable of restoring its original colour.

Cajputene, $C_{20}H_{16}$, is obtained, together with two isomeric hydrocarbons, (*isocajputene* and *paracajputene*) by cohobating bihydrate of cajputene with anhydrous phosphoric acid for half an hour, and then distilling off the liquid, whereupon cajputene passes over at 160°—165° C., isocajputene at 176°—178°, and paracajputene at 310°—316°.

Cajputene is perfectly colourless, and has a very pleasant odour resembling that of hyacinths. Sp. gr. = 0·850 at 15° C. Vapour-density by experiment 4·717; by calculation, supposing the molecule to occupy 4 volumes of vapour, it is 4·712.

Cajputene is permanent in the *air*. It is not affected by *iodine* at ordinary temperatures, but at a higher temperature, hydrogen is evolved and a black liquid is formed. *Bromine* acts quickly on it, producing a dark viscid oil. With *gaseous hydrochloric* acid, it forms a beautiful violet liquid, but no crystalline compound, even at—10° C. A mixture of ordinary *nitric* and *sulphuric acids* act upon it with violence, forming a yellow brittle resin.

Cajputene is insoluble in *alcohol*, but dissolves in *ether* and in *oil of turpentine*.

Isocajputene $C_{20}H_{16}$.—Obtained: (1.) as above. (2.) By dis-

tilling the bihydrate of cajputene with oil of vitriol. It is an oil boiling between 176° and 178° C. Its odour is less agreeable than that of cajputene, and becomes more pungent and aromatic by exposure to the air, the oil at the same time acquiring a yellow colour. Sp. gr. = 0·857 at 16° C. Vapour-density of (1) = 4·82; of (2) = 4·52.

Iodine, bromine, gaseous hydrochloric acid, and a mixture of *nitric* and *sulphuric acids,* act upon isocajputene in the same manner as on cajputene. With *oil of vitriol,* and with *dilute sulphuric, hydrochloric* or *nitric acids* (neither of which acts upon cajputene), it forms dark viscid liquids.

Isocajputene is insoluble in *water* and in *alcohol,* but mixes in all proportions with *ether* and with *oil of turpentine.*

Paracajputene $C_{40}H_{32}$.—Obtained, as above mentioned, by distilling bihydrate of cajputene with anhydrous phosphoric acid; and passes over between 310° and 316° C. It is very viscous, has a lemon-yellow colour, and in certain directions exhibits deep-blue fluorescence. Vapour-density by experiment 7·96; by calculation (4 vol.) = 9·424.

The difference between the experimental and calculated vapour-densities is probably due to decomposition, taking place at the high temperature required for the determination.

Paracajputene oxidises rapidly in contact with the *air,* acquiring a red colour and resinous consistence. A mixture of *nitric* and *sulphuric acids* does not act so violently on it as on cajputene and isocajputene. With *hydrochloric acid gas,* it forms a dark viscid liquid which does not yield crystals, even at—10° C. It is insoluble in *water, alcohol,* and *oil of turpentine;* soluble in *ether.*

Hydrates of Cajputene.—*a.* Mono-hydrate $C_{20}H_{16}.HO$.—Obtained by the action of oil of vitriol on oil of cajeput. When the crude oil is raised to the boiling point in a deep open vessel, and oil of vitriol continuously dropped into it, violent ebullition takes place, accompanied, after a while, by a peculiar crackling sound. As soon as this is observed, the flame must be lowered and the acid very cautiously added till the liquid suddenly assumes a dark colour, extending in an instant from the surface throughout the whole depth. The vessel must then be immediately removed from the fire, otherwise further decomposition will take place, attended with evolution of sulphurous acid. The upper oily liquid is separated from the acid on which it floats, then well washed, and distilled, and the portion which passes over from the 170° to 175° is collected and rectified. It is an oily liquid, having a vapour-density of 5·19 to 5·27; by calculation (4 vol.) = 5·024.

This vapour-density is anomalous, inasmuch as the molecule $C_{20}H_{17}O$, which occupies four volumes of vapour, contains but 1 atom of oxygen. Probably the true formula of the body is

$C_{40}H_{34}O_2 = C_{40}H_{32} + H_2O_2$, this molecule splitting up at high temperatures into $C_{40}H_{32}$ and H_2O_2, each of which occupies four volumes of vapour, and consequently the two together occupy 8 volumes.*

b. Bihydrate, $C_{20}H_{18}O_2 = C_{20}H_{16}.2HO$.—This is the chief constituent of oil of cajeput, and passes over in the fractional distillation between 175° and 178° C. After rectification, it is a colourless oil which boils constantly at 175°, has a specific gravity of 0·903 at 17°, and vapour-density = 5·43; the calculated vapour-density (4 vol.) is 5·38.

When exposed to the *air* for a considerable time in the moist state, it changes to a reddish liquid which ultimately exhibits a rather strong acid reaction with litmus. *Iodine* dissolves in the oil, and under certain circumstances forms crystalline compounds (p. 69). *Bromine* acts quickly upon it, and forms crystalline compounds under similar circumstances. *Chlorine gas* passed into the oil raises the temperature, but does not appear to act upon it further; but *nascent* chlorine (evolved by passing hydrochloric acid gas into the oil mixed with dilute nitric acid) converts it into bichloride of cajputene $C_{20}H_{16}Cl_2$. *Anhydrous phosphoric acid* heated with the bihydrate, takes away the whole of its water, converting it into cajputene, isocajputene, and paracajputene (p. 64). *Chloride of zinc* likewise dehydrates it, but less completely. *Strong sulphuric acid* acts but very slowly on the oil at low temperatures; but if the temperature be allowed to rise, sulphurous acid is given off, and the oil blackens and ultimately suffers complete decomposition. If the action be checked at a certain point, a sulpho-acid is formed, which yields a soluble baryta-salt. Strong sulphuric acid dropped into the oil at the boiling heat, in the manner described at page 65, takes away half the water, forming mono-hydrate of cajputene. *Dilute sulphuric acid* on the contrary causes the bihydrate to take up 4 At. more water, converting it into $C_{20}H_{16} + 6HO$. *Fuming sulphuric acid* converts the bihydrate into a thick brown liquid, which boils above 360°. *Fuming nitric acid* rapidly oxidises the oil, even at ordinary temperatures, forming a large quantity of oxalic acid. Ordinary nitric acid produces the same effect at the boiling heat, but at ordinary temperatures, it over acts very slowly, converting the oil into a red liquid. Distilled *permanganate* or *bichromate of potassium* in presence of sulphuric acid, it forms a thick resinous liquid. It does not appear to be altered by digestion with *peroxide of lead*. In contact with aqueous *potash*, or when dropped into melting potash, it forms a soluble salt, the acid of which is precipitated as a resin by hydrochloric

* See "Observations on Anomalous Vapour-densities," by Dr. Hofmann; (Proceedings of the Royal Society, vol. x, pp. 224, 596); also Gmelin's Handbook, English Edition, xiii, 487.

or sulphuric acid. Heated with *sodium*, it forms a crystalline mass, soluble in water and alcohol, and consisting of soda and an organic substance, which is separated by strong acids in the form of a fragrant resin. When the vapour of the bihydrate is passed over red hot *soda-lime*, a yellow oil distils over, having a peculiar odour quite different from that of the bihydrate, and at the same time the soda-lime becomes blackened by deposited charcoal, and when treated with acids, gives off a large quantity of carbonic acid. The yellow oil thus formed yielded by distillation a fraction boiling between 180° and 185° C., which gave in two analyses, 79·76 and 80·03 p. c. C, 12·20 and 12·07 H, agreeing nearly with the formula $C_{26}H_{24}O_{26}$ which requires 79·59 p. c. C, 12·44 H, and 7·97 O.

Bihydrate of cajputene dissolves in all proportions in *alcohol, ether,* and *oil of turpentine.*

c. Hexhydrate, $C_{20}H_{22}O_6 = C_{20}H_{16},6HO$.—Produced by the action of dilute sulphuric acid on the bihydrate, or on crude oil of cajeput. Two parts of dilute sulphuric acid are added to 1 part of the crude oil; and the mixture is well shaken for several days till the watery layer acquires a yellowish colour, and then left to itself for about ten days, whereupon it deposits crystalline tufts of the hexhydrate, adhering to the sides of the vessel.

The crystals melt at 120° C., and solidify again at 85°. On submitting them to dry distillation, an oily liquid passes over and condenses again in the colder parts of the apparatus, apparently as the unaltered hexydrate. The crystals dissolve sparingly in cold, easily in boiling alcohol.

Crystals having the same composition were deposited from a secondary fraction of crude cajeput-oil, which distilled at 216°—230° C., and was left for a very long time moist and exposed to the air. The crude oil mixed with nitric acid and alcohol, changes, in the course of seven or eight months, into a black heavy liquid in which crystals are suspended, perhaps consisting of the hexhydrate. The same compound appears likewise to be formed in beautiful long prisms, when the crystalline mass produced by passing hydrochloric acid gas into rectified oil of cajeput is thrown into water or alcohol.

Chloride of Cajputene. $C_{20}H_{16}Cl_2$.—Produced by the action of nascent chlorine on the bihydrate. When the portion of cajeput oil, distilling between 175° and 178° C., is mixed with very dilute nitric acid, and hydrochloric acid gas is passed into the liquid, a violent action takes place in a few minutes, yellow and red fumes of chlorine and nitrous gas being evolved, and if the passage of the gas be continued, chloride of cajputene ultimately sinks to the bottom, as a limpid brown oil, which may be freed from adhering nitric and nitrous acid by distillation over strong potash-ley. It has a fragrant odour, and may be kept for any length of time

without alteration, but is decomposed by distillation. Boiled with nitrate of silver, it detonates in a peculiar manner and forms chloride of silver.

Crystals were once obtained by keeping the oil at a low temperature, but not in sufficient quantity for analysis.

Monohydrochlorate of Cajputene. $C_{20}H_{16}$,HCl.—Obtained by distilling the bihydrochlorate, and collecting apart the fraction which boils at 160°.

A product having the same composition is obtained by treating the bihydrochlorate for several days with aqueous or alcoholic potash; but its odour is different from that of the product obtained by simple distillation of the hydrochlorate, and resembles that of pelargonic ether.

Bihydrochlorate of Cajputene. $C_{20}H_{16}$,2HCl.—Obtained by passing hydrochloric acid gas through rectified cajeput-oil, mixed with a third of its volume of alcohol or strong aqueous hydrochloric acid. Crystallises from alcohol in beautiful radiating tufts. Melts at 55° C., and solidifies again at 30°. It has no taste or smell. By dry distillation, it gives off hydrochloric gas at 60°, and splits into several fractions, one of which is the monohydrochlorate. It is also deprived of half its chlorine by heating with aqueous or alcoholic potash. It dissolves sparingly in cold, easily in boiling alcohol or ether.

When hydrochloric acid gas is passed through rectified oil of cajeput, kept at a low temperature, a violet liquid is formed which in 10 or 15 minutes solidifies in a crystalline mass. This crystalline compound is extremely deliquescent, liquefying rapidly even when pressed between blotting paper cooled to —25° C.; the resulting liquid rapidly gives off fumes of hydrochloric acid, and is completely decomposed by distillation. If the crystalline mass, immediately after its formation, be thrown into water or alcohol, beautiful long prisms are formed, after a few days, apparently consisting of hexhydrate of cajputene.

Bromide of Cajputene. $C_{20}H_{16}Br_4$.—Obtained by the action of bromine on oil of cajeput. When dry bromine is dropped into the rectified oil, a very brisk action takes place, and the sides of the vessel become covered with yellow needles, which however soon disappear; but if the addition of the bromide be continued till the reaction almost ceases, a dark, thick, viscous oil is formed, which, after several weeks, deposits a granular substance. By boiling the mixture with alcohol, the granular substance is extracted; a heavy oil is left behind; and the alcoholic solution, on cooling, deposits bromide of cajputene as a soft crystalline substance, having a fatty lustre and much resembling cholesterin.

Bromide of cajputene melts at 60° C, and solidifies again at 32°.

By dry distillation, it yields a liquid which crystallises again in the cooler parts of the retort. It is not altered by boiling with aqueous potash. It dissolves in ether and in boiling alcohol.

Rectified oil of cajeput shaken up with bromine-water forms a red resin, from which a solid substance separates in small white prisms, extremely deliquescent and rapidly decomposing.

Another crystallised bromine-compound (probably a hydrobromate analogous to the hydriodate), is formed in the same manner as that compound.

HYDRIODATE OF CAJPUTENE.—*a. Anhydrous,* $C_{20}H_{16}$,HI.—Obtained by adding a solution of phosphorus in bisulphide of carbon to a solution of iodine and oil of cajeput in the same liquid. Brisk action then takes place, the vessel becoming very hot; red oxide of phosphorus is precipitated; the oily liquid becomes reddish; and gives off vapours probably containing phosphurretted hydrogen, and if left to itself for 10 or 12 days, deposits crystals of the hydriodate. The reaction probably takes place as represented by the equation:

$$3C_{20}H_{16} + 3PI + 6HO = 3C_{20}H_{17}I + PH_3 + PO + PO_5$$

The crystals of the hydriodate are deposited in cells like those of beehives, and possess a black metallic lustre. They are soluble in alcohol and in ether, and are very stable, not being altered, even by boiling with potash.

b. *Hydrated,* $C_{20}H_{18}IO = C_{20}H_{16}HI + HO.$, or *Hydriodate of Monohydrate of Cajputene.* $C_{20}H_{17}O$,HI.—When iodine is added in small quantities to cajeput oil, crude or rectified, at ordinary temperatures, no visible action takes place (if external heat be applied, the action goes too far and nothing but a viscous mass is produced which does not crystallise); but on stirring rather constantly, the action is assisted, partly by the heat resulting from the friction of the glass rod, partly by the mechanical distribution of the iodine, and the temperature of the liquid soon rises from 10° to 40° C. The addition of iodine must then be discontinued, and the vessel immersed in cold water. A black crystalline compound then separates after a short time; and on separating this substance from the oily liquid by filtration, pressing it between blotting paper, and when it is nearly dry, dissolving it in alcohol or ether, a solution is obtained, from which the hydrated hydriodate crystallises in prisms having a fine yellow-green colour and metallic lustre. They are very deliquescent, and melt at 80° C. into a liquid which does not recrystallise in the cold. Potash-ley liquefies the compound, abstracting part of the iodine, and with the aid of heat abstracts the whole.

It is insoluble in *water,* and is not decomposed thereby; very soluble in *alcohol* and *ether.*

On the Basic Carbonates of Copper.

By Frederick Field.

On adding sulphate of copper to a great excess of solution of sesquicarbonate of soda, no precipitate is obtained until a considerable quantity of the copper-salt has been introduced. Even then, on gently warming, the small precipitate of carbonate of copper is dissolved, forming a bright blue solution. When this liquid is boiled for some time, a green granular precipitate is obtained, the supernatant liquid still holding copper in solution with great tenacity, and maintaining its clear blue colour. If the ebullition has not been continued for more than half an hour, on filtering the liquid from the precipitate, the former is found to be capable of dissolving a further quantity of copper, which is precipitated as a green powder similar to the last. After very protracted ebullition, however, the filtrate from this last precipitate yields, on the introduction of sulphate of copper, not a green powder, but one of a dense black colour.

Composition of the Green Precipitate.—After thorough washing, the green compound was dried on a water-bath until it ceased to lose weight, and the copper and carbonic acid were determined, the water being estimated as loss.

	I.	II.
Copper	57·46	57·21
Carbonic acid	19·45	19·31

This compound is identical in composition with the ordinary green dicarbonate and malachite, as shown by the following numbers, which, for the sake of comparison, are placed in juxtaposition with the results obtained in the analysis of a fine specimen of pure malachite from the west coast of Africa, and some beautiful crystals of native dicarbonate of copper from Chili.

	Green Precipitate.	Malachite.	Crystals.	Calculated.
CuO	71·81	71·74	71·69	72·06
CO_2	19·45	19·68	19·80	19·82
HO (loss)	8·74	8·58	8·51	8·12
	100·00	100·00	100·00	100·00

Composition of the Black Precipitate.—This compound, after boiling with the strongly alkaline liquid for a considerable time, was washed and dried in a water-bath.

On analysis, it was found to consist of 4 equivalents of oxide combined with one of dicarbonate of copper, or, which is the same thing, 6 of oxide of copper and 1 of carbonic acid, as the following numbers will show:

	Found.		Calculated.
	I.	II.	
CuO	91·42	91·39	91·60
CO_2	8·44	8·51	8·40

Very long protracted boiling of the alkaline liquid was necessary to convert this compound into oxide of copper. Suspended in pure boiling water, it is decomposed in a few minutes.

When powdered malachite is introduced into boiling water, the mineral blackens in a few minutes, and after half an hour's brisk ebullition, is entirely converted into black oxide. Artificially prepared dicarbonate suffers the same reaction. When equivalent proportions of sulphate of copper and carbonate of soda are dissolved in water, the ultimate result is the same, although much retarded by the sulphate of soda in solution. I could obtain no decomposition of either the mineral or the artificial compound in a boiling solution of chloride of sodium.

When sulphate of copper is gradually added to a strong solution of carbonate of soda an immediate blue precipitate occurs, on the addition of the first few drops, unaccompanied by effervesence, and by the further introduction of the copper-salt, no more precipitation takes place, but a dark blue solution is formed. When this is heated, it immediately darkens, owing to the formation of a black powder. The addition of sulphate of copper to the supernatant carbonate of soda causes a bright temporary blue colour which is almost instantaneously changed into the black. Washed and dried this substance was found to contain:

	I.	II.
CuO	91·49	91·52
CO	8·38	8·41

and thus to have the same composition as the one mentioned above, viz.: $4CuO,2CuO,CO_2$. This highly basic carbonate can be boiled with carbonate of soda for many hours without decomposition; suspended in pure boiling water it is speedily decomposed.

Action of Carbonate of Soda upon Dicarbonate of Copper. When a solution of carbonate of soda is heated, even only to the temperature of 120°F, and powdered malachite or artificial dicarbonate is introduced, decomposition quickly takes place, as is shown by the darkening of the compounds. An evolution of carbonic acid always accompanies the reaction. A few minutes boiling yields the compound $4CuO, 2CuO,CO_2$.

It may further be remarked that when dicarbonate of copper either artificially prepared or as malachite, is boiled with a solution of sesquicarbonate of soda, it is dissolved and a blue solution is formed which is not decomposed, after long ebullition, sesqui-

carbonate of soda containing carbonate of copper in solution appearing to resist the action of heat far more strongly than it does in the absence of the latter metal.

When sulphate of copper is added to a mixed solution of a sesquicarbonate and sulphite of soda, no precipitate is formed. An easy and safe method of de-oxidation consists in adding a mixture of about equal parts of sesquicarbonate and sulphite of soda to a hot solution of a proto-salt of copper. After heating for some little time, the introduction of a slight excess of hydrochloric acid produces a solution which is perfectly colourless, and gives with potash the clear orange precipitate of the suboxide, and with ammonia no blue shade if the air be carefully excluded. With regard to the precipitation of copper from its various salts, as protoxide, it is much better to employ hypochlorite of soda, than caustic potash. The precipitate subsides more quickly, and is infinitely easier to wash.

Contributions to the History of the Phosphorus Bases.

By Augustus William Hofmann, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

SECOND MEMOIR.

Theory of Diatomic Bases. Diphosphonium-Compounds.

In surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot avoid recognizing as one of the most valuable amongst these acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the classical researches of Graham and Liebig on the polybasic acids, and afterwards extended and generalized by the experiments of Gerhardt and Williamson, it has acquired in Berthelot's beautiful investigation of glycerin, a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. Buff, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation, until, in the brilliant experimental researches of Wurtz, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination.

Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained. For, as from a single molecule of water, a monatomic alcohol, a monobasic acid, or a monacid base can be produced, according to the nature of the monatomic radical by which the hydrogen is replaced, so likewise must it be possible, by a proper

selection of polyatomic radicals to link two or more molecules of water, so as to form one molecule of a polyacid base, just as the introduction of other polyatomic radicals gives rise to the formation of polyatomic alcohols or polybasic acids. It remained only to submit these ideas to the test of experiment.

Material for building up this group of bodies appeared to present itself unmistakeably in the chlorine-, bromine-, and iodine-compounds of ethylene and its homologues. Having succeeded some years ago in converting the corresponding ethyl-compounds by the action of ammonia into the monacid ethyl-bases, I was justified in expecting that by treating the ethylene-compounds with ammonia, diacid bases might be formed. Respecting some of the bodies which are produced in these reactions, investigations had already been published by Cloëz,* and more recently by Natanson,† whose results appeared at first sight to give but little encouragement to any such attempt. But a careful examination of these researches soon convinced me that, at the time when they were undertaken, chemical knowledge had not sufficiently advanced to afford a correct interpretation of the results elicited.

I have once more studied these reactions, and have obtained experimental confirmation of the correctness of my anticipations. But the action of ammonia on the chloride, bromide, and iodide of ethylene presents unexpected complications, quite independent of those indicated by theory, and for which I was not altogether prepared.

Consider for a moment the manner in which the reaction between ammonia and a diatomic bromide—dibromide of ethylene for instance—may take place. Just as bromide of ethyl, acting, as it does, on a single molecule of ammonia, gives rise to the formation of the four bromides,

$$[(C_2H_5)\ H_3N]Br,‡$$
$$[(C_2H_5)_2H_2N]Br,$$
$$[(C_2H_5)_3H\ N]Br,$$
$$\text{and } [(C_2H_5)_4\quad N]Br,$$

so likewise may dibromide of ethylene, acting on two molecules of ammonia, be expected to produce four diatomic bromides, viz.—

$$[(C_2H_4)''\ H_6N_2]''Br_2,$$
$$[(C_2H_4)_2''H_4N_2]''Br_2,$$
$$[(C_2H_4)_3''H_2N_2]''Br_2,$$
$$\text{and } [(C_2H_4)_4''\quad N_2]''Br_2.$$

These, however, are by no means the only compounds which, in accordance with our present conception of diatomic compounds, may be formed in this reaction.

It appears from the researches of Wurtz, that dibromide of ethylene does not pass into ethylene-alcohol at a single bound, but

* Instit. 1853, p 213. † Ann. Ch. Pharm. xcii. 48, and xcviii. 291.
‡ H=1; O=16; S=32; C=12, &c.

that there exists an intermediate member of the series still containing half the bromine.

$(C_2H_4)''\left\{\begin{matrix}Br\\Br\end{matrix}\right.$ Dibromide of Ethylene. $(C_2H_4)''\left\{\begin{matrix}Br\\HO\end{matrix}\right.$ Intermediate Bromide. $(C_2H_4)''\left\{\begin{matrix}HO\\HO\end{matrix}\right.$ Ethylene-alcohol.

There could, therefore, be no doubt that dibromide of ethylene would, under certain conditions, likewise react with ammonia as a monatomic compound, giving rise to another series of bodies in which the hydrogen would be more or less replaced by the monatomic radical C_2H_4Br, viz.—

$$\begin{matrix}[(C_2H_4Br)\ H_3N]Br,\\ [(C_2H_4Br)_2H_2N]Br,\\ [(C_2H_4Br)_3H\ N]Br,\\ \text{and } [(C_2H_4Br)_4\ \ N]Br.\end{matrix}$$

Further, if the reaction took place in presence of water, it was to be expected that the bromine, wholly or partially eliminated as hydrobromic acid, would be replaced by the molecular residue of the water; and thus, independently of any mixed compounds containing bromine *and* oxygen, a series of salts might be looked for, in which a molecule $C_2H_4HO=C_2H_5O$ would enter monatomically, viz.—

$$\begin{matrix}[(C_2H_5O)\ H_3N]Br,\\ [(C_2H_5O)_2H_2N]Br,\\ [(C_2H_5O)_3H\ N]Br,\\ \text{and } [(C_2H_5O)_4\ \ N]Br.\end{matrix}$$

Lastly, remembering the tendency exhibited by ethylene-compounds to resolve themselves, in presence of alkalies, into vinyl-compounds, it appeared not improbable that a fourth series of bodies would likewise be formed, viz.—

$$\begin{matrix}[(C_2H_3)\ H_3N]Br,\\ [(C_2H_3)_2H_2N]Br,\\ [(C_2H_3)_3H\ N]Br,\\ \text{and } [(C_2H_3)_4\ \ N]Br;\end{matrix}$$

and thus was presented the not very inviting problem of separating from a great mass of bromide of ammonium, no fewer than sixteen different bases.

In the experiments on the action of dibromide of ethylene on ammonia and its homologues, which I intend to publish in a special paper, I have indeed by no means met with the whole of these compounds; but in place of the deficient members of the groups, new products have made their appearance, whose formation in the present state of our knowledge could scarcely have been predicted. Without entering into details respecting these products, I will merely observe that I was induced, by the complication of this reaction, to subject dibromide of ethylene to the

action of ethylamine, diethylamine, and finally of triethylamine instead of ammonia; for it could not be doubted that with the progressive substitution of ethyl for the hydrogen in ammonia, the process would be simplified, the number of possible products of reaction being considerably diminished. Ammonia indeed—omitting secondary products—is capable of producing not less than *sixteen* compounds, whereas ethylamine cannot yield more than *twelve*, diethylamine not more than *eight*, and in the reaction between triethylamine and dibromide of ethylene, the number of compounds possible under the most favourable circumstances is limited to *four*. Experiment has verified this anticipation; in the same proportion as the substitution advances in the ammonia submitted to the action, the number of products generated diminishes; nevertheless the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus-series, using, instead of triethylamine, the corresponding phosphorus-base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory, undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness; and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality, such as I have never observed in any similar reaction among bodies of the nitrogen-series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus-series.

Ethylene-Group.

Action of Dibromide of Ethylene on Triethylphosphine.

When these two bodies are brought together in quantities not too large, the liquid becomes turbid, but no rise of temperature takes place to indicate the occurrence of chemical action. The mixture, after being left to itself for a few hours, deposits white crystals, the formation of which continues till the entire liquid is converted into a white saline mass. If the mixture be even gently heated, the crystallization takes place instantaneously, and a violent reaction sets in, which is very apt to project a portion of the resulting salt from the vessel. In operating on rather a large scale in vessels filled with air, the heat evolved on agitation, in consequence of the oxidation of the phosphorous-base, is often sufficient to start the reaction.

In preparing considerable quantities of the white crystals, I have therefore found it convenient to add to the triethylphosphine twice its volume of ether, to mix the ethereal solution with the dibromide of ethylene in a flask filled with carbonic acid gas, and to heat the mixture in a water-bath, the flask being provided with an inverted cooling apparatus, so that the vapours which escape may be condensed and returned. Or, the mixture of triethylphosphine, dibromide of ethylene and ether may be introduced into long tubes previously drawn out, and the tubes, after sealing, immersed for some hours in boiling water. As the value of dibromide of ethylene is trifling in comparison with that of triethylphosphine, I always, in commencing the study of this reaction, used the former substance in excess. The triethylphosphine is quickly fixed by the dibromide of ethylene, and the action may be considered as terminated when the presence of the free phosphorus-base in the mixture is no longer indicated by disulphide of carbon. As soon as this point is attained, the crystalline bromides may be thrown on a filter, the ether allowed to drain off, and the crystals freed from excess of bromide of ethylene by washing them for a while with anhydrous ether, in which they are quite insoluble.

The crystals thus obtained dissolve with great facility in water and in ordinary alcohol, somewhat less readily in boiling absolute alcohol. This solution on cooling deposits well-developed crystals, which sustain a heat of 100°C without decomposition, but show a slight tendency to deliquesce in the air. The analysis of these crystals, and their behaviour with reagents, showed unmistakeably that, in the action of dibromide of ethylene on triethylphosphine, at least two bromides are formed. The determination of the bromine by means of nitrate of silver in the products of different preparations, purified by successive crystallizations from alcohol, gave percentages of bromine varying from 32·1 to 25·94. On again repeating the crystallization, the amount of bromine precipitated by nitrate of silver did not exhibit any further diminution.

The complete analysis of the crystals, purified by a great number of crystallizations from alcohol, has led me to the simple expression

$$C_8H_{19}PBr_2 = C_6H_{15}P + C_2H_4Br_2,$$

whence it appears that the body is produced by the combination of one molecule of triethylphosphine with one molecule of the bromine-compound.

The purification of the second substance, yielding with nitrate of silver a larger proportion of bromine, which remains in the mother-liquor of the compound just described, is somewhat complicated. As I shall have to return to this body in the description of the individual compounds, I content myself in this place with just setting forth the general character of the reaction by quoting the formula deduced from its examination. The analysis of this

bromine-compound, together with those of a whole series of bodies derived from it, has led to the formula

$$C_{14}H_{34}P_2Br_2 = 2C_6H_{15}P + C_2H_4Br_2,$$

showing that the body is a compound of two molecules of triethylphosphine and one molecule of dibromide of ethylene.

These observations are sufficient to establish the peculiar nature of the reaction in question. There are clearly two successive phases to be distinguished, according as the bromide of ethylene lays hold of one or two molecules of triethylphosphine; secondary products may likewise be formed, which for the present may be left out of consideration, as I shall have to allude to them in the course of the memoir. It is, however, worth while to mention in this place that, when the experiment is made with pure substances, and under the conditions above mentioned, the two bromides described are almost the only products of the reaction.

These two bodies have become the starting-points of two extensive groups of compounds, which may even now be distinguished as the *series of monatomic compounds*, and the *series of diatomic compounds*.

I now proceed to the detailed description of the individual members of these series.

Series of Monatomic Compounds. Monophosphonium-Compounds.

Salts of Bromethyl-triethylphosphonium.

Bromide of Bromethyl-triethylphosphonium.—By this long name I designate the crystalline substance which is produced by the union of one molecule of dibromide of ethylene and one molecule of triethylphosphine. The preparation of this compound has already been given in the preceding paragraph. It is the chief product of the reaction when the dibromide of ethylene is in excess.

The equation

$$C_2H_4Br_2 + C_6H_{15}P = C_8H_{19}PBr_2$$

requires about 1 vol. of dibromide of ethylene to 1·5 vol. of triethylphosphine; but even when a larger quantity of the bromine-compound is *heated* with the phosphorus-base, either in presence or absence of ether or alcohol, we always obtain an appreciable quantity of the second bromide. It is only by allowing an *immense* excess of dibromide to act at the *common temperature* upon triethylphosphine, either in presence or absence of ether, that the formation of the second bromide is altogether avoided. In this reaction, which is not complete in less than twenty-four hours, a considerable quantity of gas is evolved, which does *not* appear when the substances are heated together.

To purify the product, which contains appreciable quantities of the second bromide, it is necessary to crystallize it at least three or

four times from absolute alcohol; in the last crystallization it is desirable to mix the alcoholic solution with a moderate quantity of ether. The solution, if left to itself, frequently deposits separate well-defined crystals, which may be dried without decomposition at 100°, and which melt at about 235° C with partial decomposition, hydrobromic acid being abundantly evolved.

A simple experiment showed that nitrate of silver precipitates from this compound only part of the bromine. When the liquid filtered from the precipitated bromide of silver was mixed with carbonate of sodium, to remove the excess of silver, and evaporated, the residue, when ignited with lime and dissolved in nitric acid, gave, on addition of nitrate of silver, a fresh quantity of bromide of silver. I therefore endeavoured to obtain the entire quantity of bromine by means of recently precipitated oxide of silver, a process which I had previously found serviceable in similar cases. The result confirmed my anticipation. Digestion with oxide of silver removes the whole of the bromine, and shows that the quantity precipitated by nitrate of silver is only half the total amount.

The analysis* of this substance led to the formula, already quoted,

$$C_8\ H_{19}P\ Br_2,\dagger$$

the interpretation of which presents no difficulty. The crystals are evidently the bromide of a monophosphonium in which 3 eqs. of ethyl are substituted for 3 equivs. of hydrogen, the last equivalent of hydrogen being replaced by a secondary radical, C_2H_4Br, which for the present I will call *monobrominated ethyl* or *bromethyl*.

The molecular formula

$$[(C_2H_4Br)\ (C_2H_5)_3P]\ Br$$

represents the constitution of this salt.

I have already observed that this bromide is occasionally obtained in well-defined crystals. They were examined by Quintino Sella:

"System monometric (regular).

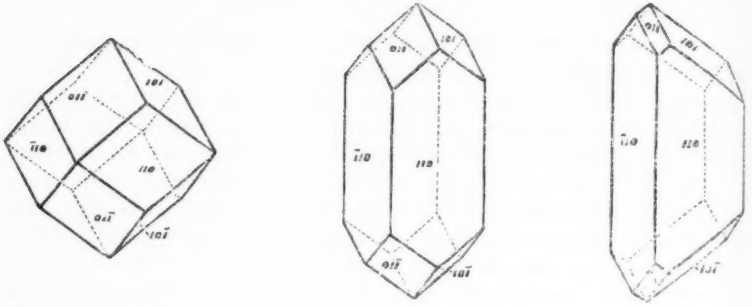
The crystals exhibit the form of the rhombic dodecahedron 110 (Fig. 28).‡ They are sometimes elongated so as to present the aspect of dimetric crystals, as in Fig. 29. Sometimes it even happens that one of the faces $\bar{1}\ 1\ 0$ is much more developed than the parallel face $1\ \bar{1}\ 0$ (Fig. 30), so that scarcely more than half the crystal (Fig. 29) appears to exist. Sometimes the faces exhibit striæ parallel to the adjacent edges of the rhombic dodecahedron.

* The details of the analytical determination are given in the original papers published in the Philosophical Transactions for 1860.

† H=1; O=16; S=32; C=12.

‡ The figures are numbered consecutively, with that in Dr. Hofmann's former paper on the phosphorus bases, vol. xiii, p. 289, of this Journal.

Fig. 28. Feb. 29. Fig. 30.



Lustre fatty.

Hardness inferior to that of gypsum.

The crystals have no action on polarized light."

By treating the bromide with silver-salts *in the cold*, the bromine external to the phosphonium-metal is replaced by the acid-radical united with the silver, while the bromine belonging to the phosphonium remains untouched. In this manner, we obtain the salts of the new metal, which exhibit an inclination to unite with excess of the silver-salts, in the form of double compounds. The *chloride* and the *nitrate* prepared from the bromide by the action of chloride and nitrate of silver are extremely soluble in water and alcohol, and crystallize indistinctly. The *sulphate* forms long white crystalline needles, likewise very soluble in water and alcohol. It is very easily obtained by the action of sulphuretted hydrogen on the double salt which is formed by treating the bromide with sulphate of silver; on adding alcohol and ether to the concentrated liquid containing free sulphuric acid, it is precipitated in crystals. The sulphate, treated with iodide of barium, yields the *iodide*, a salt which dissolves sparingly in water, and crystallizes in scales of a pearly lustre.

I have not examined these salts more particularly, as they scarcely present any theoretical interest, and as the composition of the bromide, which forms the starting-point of the series, is sufficiently corroborated by the analysis of the platinum- and gold-salts.

Platinum-salt.—The chloride obtained by digesting the bromide with excess of chloride of silver is mixed with dichloride of platinum, when the platinum-salt is deposited on cooling in light orange-yellow prisms, frequently an inch in length. This salt is somewhat sparingly soluble in cold, more readily in boiling water, and may be crystallized without decomposition. During the recrystallizations, this salt, under circumstances not yet clearly made out, is occasionally obtained in crystals of an octahedral habitus.

This platinum-salt, though somewhat sparingly soluble, is nevertheless essentially different from the platinum-salt of the

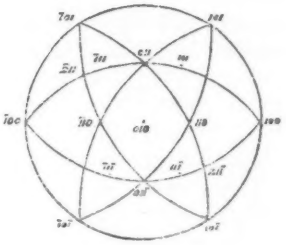
diphosphonium to be described hereafter, which accompanies the bromethyltriethyl-phosphonium. The latter is nearly insoluble in water, and is precipitated from the most dilute solutions. This character forms a means of testing the purity of the monophosphonium-bromide in the succession of crystallizations to which it has to be submitted for the sake of purification. The salt is pure when the dilute solution after being treated with chloride of silver, no longer gives a precipitate with dichloride of platinum.

The platinum salt contains :—

$C_8H_{19}Br\ P\ Pt\ Cl_3 = [(C_2H_4Br)\ [(C_2H_5)_3P]\ Cl, Pt\ Cl_2$.

The crystalline form was likewise determined by Quintino Sella.

Fig. 31.



"System monoclinic :—

100, 101=55° 59′; 001, 101,= 33° 3′; 010, 111=60° 37′.

Forms observed:—

100, 010, 110, 101, $\bar{1}01$, 011, 111, $\bar{1}11$, $\bar{2}11$ (Fig. 31).

Fig. 32.

Fig. 33.

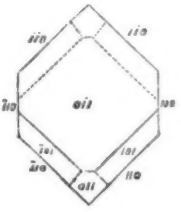
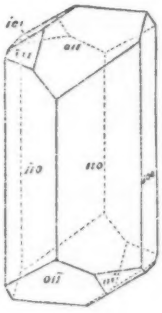


Fig. 34.



Combinations observed :—

110, 011, 100; 101, $\bar{1}01$ (Figs. 32, 33).
110, 011; 100, $\bar{1}11$, $\bar{1}01$ (Fig. 34).
110, 011; 100, $\bar{1}11$, $\bar{1}01$, $\bar{2}11$ (Fig. 35).
110, $\bar{1}11$; 100, $\bar{1}01$, 011, 111 (Fig. 36).
110, 011, 100, 111; 101, $\bar{1}11$, $\bar{2}11$ (Fig. 37).
110, 011, 100; 010, 011, $\bar{1}01$, 211 (Figs. 38, 39).

Fig. 35.

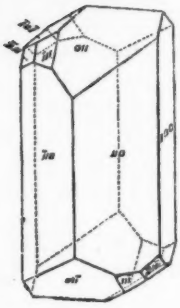
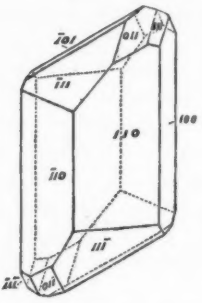


Fig. 36.



The faces 0 1 1 are often very irregularly developed, as seen in Figs. 32, 33, and 38, 39; under these circumstances some of the faces of the forms 1 1 1, $\bar{1}$ 1 1, $\bar{2}$ 1 1 are apt to disappear, as may be seen in Figs. 38 and 39.

Fig. 37.

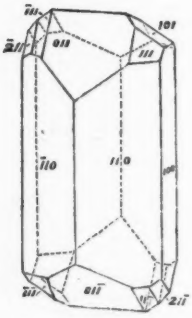


Fig. 38.

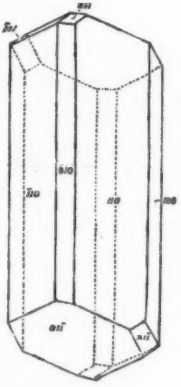
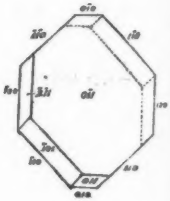


Fig. 39.



Cleavages: 1 0 0, 1 1 0.

Colour: orange with a tint of yellow in minute, and of red in larger, crystals.

The plane of the optical axes is parallel to the axis of symmetry [0 1 0]: for rings are observed across the faces of the prism 1 1 0 symmetrically with [0 1 0]."

Gold-salt.—Light yellow needles, difficultly soluble in cold water, recrystallizable from boiling water, containing

$$C_8H_{19}Br\,P\,Au\,Cl_4 = [(C_2H_4Br)\,(C_2H_5)_3P]\,Cl_3,\,Au\,Cl_3.$$

I have in vain endeavoured to prepare the hydrate

$$C_8\,H_{20}\,Br\,P\,O = \left.\begin{matrix}[(C_2\,H_4\,Br)\,(C_2\,H_5)_3\,P]\\ H\end{matrix}\right\} O$$

belonging to these salts.

In quoting the analysis of the bromide, I have already mentioned that this salt, when treated with oxide of silver, gives up the whole of its bromine. On mixing the caustic liquid filtered from the silver-salt with hydrochloric acid and dichloride of platinum, we no longer obtain the sparingly soluble platinum-double salt crystallizing in the characteristic needles; but the liquid, after being considerably concentrated by evaporation, yields well-defined, reddish-yellow octahedra belonging to another base. An exactly similar result is obtained on attempting to separate the base from the sulphate by means of baryta. After filtering off the sulphate of barium, there remains a strongly alkaline liquid, which likewise yields only the octahedral platinum-salt, while the presence of bromide of barium in the solution indicates the transformation of the original molecular system. The elimination of the second equivalent of bromine by silver-salts, which takes place instantly and completely in alkaline liquids, may likewise be effected by continual ebullition in neutral and even in acid solutions, though always slowly and incompletely. If the bromide be precipitated by excess of nitrate of silver, the filtered liquid, on being boiled and evaporated, deposits a fresh quantity of bromide of silver; but in most cases, even after long-continued boiling, a considerable quantity of bromine remains latent and may be immediately recognized by again filtering the liquid and slightly supersaturating it with ammonia, the whole of the remaining bromine being then precipitated as bromide of silver. This deportment furnishes in fact a characteristic distinction of the bromethylated bromide, by which this substance may often be conveniently recognized. It deserves to be remarked that the fixed caustic alkalies exert but a slight action on the bromethylated bromide; the compound is precipitated by the alkalies from its cold aqueous solution in the crystalline state and without decomposition, and it is only after some time that alterations take place, probably affecting its intimate constitution. The nature of these alterations has not yet been made out. The crystals may be boiled for some time with alcoholic solution of potassa without decomposition. The bromide likewise suffers no alteration by continued digestion with water or alcohol at 100°.

Salts of Oxethyl-triethylphosphonium.

Iodide.—When the caustic liquid produced by treating the bromide of bromethyl-triethylphosphonium with oxide of silver is neutralized with hydriodic acid and the solution evaporated, an iodide is obtained which crystallizes in needles, and dissolves very readily in water and alcohol. The finest crystals are obtained by mixing the alcoholic solution with ether till it becomes opalescent, and then allowing it to crystallize. If too much ether has been added, the new iodide is precipitated as an oil, which solidifies but

slowly to a crystalline mass. The salt becomes coloured at 100°, and must therefore be dried for analysis *in vacuo*. It was found to contain :—

$$C_8H_{20}OPI = [(C_2H_5O)]\ (C_2H_5)_3P]I.$$

The transformation of the bromethylated phosphonium takes place, therefore, exactly as might be expected from analogy, the bromine being eliminated as bromide of silver, and its place being taken by the molecular residue of the water :—

$$[(C_2H_4Br)\ (C_2H_5)_3P]Br + Ag_2O + H_2O = 2AgBr + \left.\begin{matrix}[(C_2H_5O)\ (C_2H_5)_3P] \\ H\end{matrix}\right\} O.$$

Hydrate.—The caustic solution of the oxide exhibits the usual characteristic properties of this class of bodies. Over sulphuric acid, the solution thickens to a syrupy, extremely deliquescent mass, from which the base separates in oily drops on addition of potassa. Its decomposition by heat is characteristic; at a rather high temperature, it is resolved into oxide of triethylphosphine, ethylene, and water :—

$$\left.\begin{matrix}[(C_2H_5O)\ (C_2H_5)_3P] \\ H\end{matrix}\right\} O = (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The oxide of triethylphosphine was identified by the preparation of its platinum-salt; the ethylene, by converting it into the bromide.

The above equation represents the final result of the action of heat; this final result, however, is preceded by several intermediate changes, to which I shall return in a subsequent section of this paper.

Bromide.—Extremely soluble. Dries up over sulphuric acid to an indistinct crystalline mass.

Chloride.—This compound resembles the bromide in every respect. Both these salts readily form double compounds with iodide and bromide of zinc. The chloride, under the influence of pentabromide and pentachloride of phosphorus, undergoes remarkable transformations, to which I shall presently recur.

Perchlorate.—Laminæ somewhat sparingly soluble in cold water.

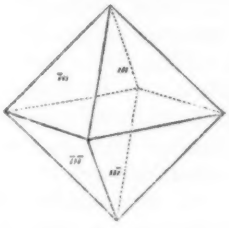
I have not analysed any of these salts, inasmuch as the composition of this series of compounds is, moreover, sufficiently established by the analysis of the platinum- and gold-salt.

Platinum-salt.—The alkaline solution, from which the iodide was obtained, yields, when saturated with hydrochloric acid, mixed with dichloride of platinum, and evaporated, the above-mentioned platinum salt, containing—

$$C_8H_{20}OPPtCl_3 = [(C_2H_5O)\ (C_2H_5)_3P]\ Cl,\ PtCl_2.$$

This salt is easily soluble in boiling water, and may be recrystallized without decomposition. It forms splendid octahedra, which were measured by Quintino Sella:

Fig. 40.



"System monometric:—

Form observed:—

111 (Fig. 40.)

No sensible influence on polarized light. Colour orange."

Gold-salt.—Golden-yellow needles, sparingly soluble in cold, readily in boiling water: in a quantity of boiling water not sufficient to dissolve them, they fuse to a transparent yellow oil. Not decomposed by recrystillization. Precipitated by trichloride of gold from a moderately concentrated solution of the chloride. Analysis led to the formula:

$$C_8\ H_{20}\ O\ P\ Au\ Cl_4 = [(C_2\ H_5\ O)\ (C_2\ H_5)_3\ P]\ Cl,\ Au\ Cl_3.$$

I have already alluded to the decomposition which the chloride of the oxethylated phosphonium undergoes under the influence of pentabromide of phosphorus. The two bodies act upon one another with great violence: oxybromide of phosphorus and hydrobromic acid are evolved, and the residue is found to contain the chloride of the bromethylated phosphonium from which the oxethylated compound was originally produced.

$$[(C_2H_5O)\ (C_2H_5)_3P]Cl + PBr_5 = POBr_3 + HBr) + [(C_2H_4Br)\ (C_2H_5)_3P]Cl.$$

Nothing is easier than to obtain experimental proof of this transformation, which is of considerable theoretical interest. After the oxybromide and the excess of pentabromide have been removed as completely as possible by evaporation, the remaining liquid yields, on addition of dichloride of platinum, a sparingly soluble, still impure platinum-salt, which, after washing, may be decomposed by sulphuretted hydrogen and thereby purified. If the chloride thus formed be precipitated with excess of nitrate of silver, and the nitrate of the base, filtered from the chloride of silver, be mixed with ammonia and gently heated, a copious precipitate is immediately formed, consisting of bromide of silver. This reaction is characteristic of the bromethylated body. Moreover, on mixing the solution of the nitrate freed from silver with dichloride of platinum, and recrystallizing the platinum-precipitate from boiling water, the liquid yields on cooling the splendid needles of the platinum-salt of the bromethylated triethylphosphonium. The analysis of this salt was omitted, partly because no doubt could be entertained respecting its nature, and partly because I had occasion to establish by a number—as will be

noticed hereafter—the nature of the precisely similar reaction between chloride of oxethyl-triethylphosphonium and pentachloride of phosphorus.

Thus it is seen that the molecular group C_2H_5O, which is supposed to replace the hydrogen in the salt, suffers, under the influence of pentabromide of phosphorus, alterations exactly similar to those which it would have undergone under similar circumstances when conceived as a constituent of alcohol.

If we consider the facility with which the bromethylated phosphonium is converted into the oxethylated compound by the action of oxide of silver, and the simple re-formation of the first-mentioned body by means of pentabromide of phosphorus, a great variety of new experiments suggest themselves. In reviewing the relations which obtain between the bromethylated and oxethylated phosphoniums, who could fail to perceive that the two hydrogen-replacing radicals, which constitute the difference between these two organic metals, stand to one another in the same relation as bromide of ethyl and alcohol, or bromide of acetyl and acetic acid? But if this be so, what a number of new bodies does this consideration bring into view, even if we limit our calculation to the transformations of which the molecular group C_2H_5O in alcohol is susceptible! As yet I have scarcely penetrated into this new field of inquiry, and I must be satisfied to quote a single experiment, which exhibits the above-mentioned bodies in a new light.

The salts of bromethylated and oxethylated triethylphosphonium may be regarded as tetrethylphosphonium salts, in which an atom of hydrogen is replaced by bromine and the radical H O respectively:

Bromide of:

Tetrethylphosphonium . . .	$[C_2H_4H)\ (C_2H_5)_3P]Br$,
Bromethylated triethylphosphonium	$[(C_2H_4Br)\ (C_2H_5)_3P]Br$,
Oxethylated triethylphosphonium .	$[(C_2H_4HO)\ (C_2H_5)_3P]Br$,

and the question arose whether the bromethylated salt might not be converted by a simple process into the tetrethylphosphonium-compound. This transformation may indeed be effected without the slighest difficulty. On acidulating the solution of the bromethylated bromide with sulphuric acid, and digesting it with granulated zinc, the bromine is eliminated in the form of hydrobromic acid, its place being filled up by one equivalent of hydrogen:

$$[(C_2H_4Br)\ (C_2H_5)_3P]Br + 2H = HBr + [(C_2H_5)_4P]Br.$$

By decanting the liquid from the excess of zinc and treating it with oxide of silver, oxide of zinc, bromine and sulphuric acid are removed, and a solution of oxide of tetrethylphosphonium is obtained, which, when mixed with hydrochloric acid and dichloride

of platinum, yields well-developed octahedra of the platinum-salt of tetrethylphosphonium.

The chloride obtained in the analysis was converted, by successive treatment with oxide of silver and hydriodic acid, into the corresponding iodide. This characteristic salt appeared on careful comparison exactly similar to the iodide of tetrethylphosphonium prepared in the ordinary way.

Here, then, we have an instance of the direct reproduction of an ethyl-compound from a body of the ethylene-group by a simple process of reduction. Similar transformations would doubtless succeed in many other cases, and this is perhaps a fitting opportunity of directing attention to the interest which the employment of this reaction would have in connection with the intermediate hydrochloric glycol-ether discovered by Wurtz. Probably this compound, when subjected to the action of nascent hydrogen, would be directly converted into alcohol:

$$(C_2H_4)'' \begin{cases} HO \\ Cl \end{cases} = C_2H_5ClO,$$

$$(C_2H_4)'' \begin{cases} HO \\ H \end{cases} = C_2H_6O;$$

and when considered with reference to this decomposition, would appear as monochlorinated alcohol.

It was chiefly the facility with which a tetrethylphosphonium-compound may be obtained from the bromethylated bromide that induced me to designate the hydrogen-replacing molecules C_2H_4Br and C_2H_5O, which we meet with in the compounds above described, as *bromethyl* and *oxethyl*. I was anxious to submit the ideas which guided me in the selection of these terms to the test of experiment. We know from the experiments of Regnault, that dichloride of ethylene and monochlorinated chloride of ethyl are essentially different bodies; and not less distinct are dibromide of ethylene and monobrominated bromide of ethyl, which I have obtained in the course of these experiments by the action of bromine on bromide of ethyl. But, on the other hand, the allied members of these two pairs of bodies are so closely related to each other, that, under the influence of powerful reagents, they not unfrequently yield exactly the same products of transformation. I may here refer especially to an interesting experiment of Beilstein, who has shown that dichloride of ethylene and monochlorinated chloride of ethyl, when treated with alcoholic potassa, undergo the same decomposition: both these compounds give up hydrochloric acid, being converted into chloride of vinyl.

The denomination, *bromethyl-triethylphosphonium*, which I have adopted for the metal produced by the action of dibromide of ethylene on triethylphosphine, involves to a certain extent the assumption that this body might, under favourable circumstances,

be produced also by the mutual action of triethylphosphine and monobrominated bromide of ethyl. In a subsequent chapter of this inquiry I shall have an opportunity of showing how far this assumption is established by experiment.

SALTS OF VINYL-TRIETHYLPHOSPHONIUM.

In tracing the history of the salts of bromethyl-triethyl-phosphonium, I have mentioned that these substances lose their latent bromine, though slowly, when boiled with silver-salts. I was curious to ascertain whether this reaction involves the same metamorphosis that the bromethylated body undergoes under the influence of oxide of silver.

In the anhydrous condition, the bromethylated bromide acts but slowly on acetate of silver. In the presence of alcohol or water, the reaction is rapidly accomplished at 100° C. The liquid filtered from the bromide of silver yields no further precipitate on addition of ammonia, showing that the whole of the bromine is eliminated. When evaporated with hydrochloric acid, the liquid abundantly evolves acetic acid. After sufficient concentration, it yields with dichloride of platinum a fine octahedral salt, which may be purified by crystallization. This salt contains:

$$C_8H_{18}PPtCl_3 = [(C_2H_3)(C_2H_5)_3P]Cl, PtCl_2,$$

It is thus seen that the action of silver-salts—at all events of acetate of silver—upon the bromethylated bromide differs from that of oxide of silver. While the latter gives rise to the formation of an oxethylated phosphonium, the former produces a phosphoretted metal in which three atoms of ethyl are associated with one atom of the radical C_2H_3, which may be termed vinyl. The product, then, which is formed by the action of acetate of silver upon the bromethylated bromide is the acetate of vinyl-triethylphos-phonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + 2\left(\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O\Big) = 2AgBr + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O +$$
$$\left.\begin{matrix}C_2H_3O\\[(C_2H_3)(C_2H_5)_3P]\end{matrix}\right\}O.$$

I have been satisfied to establish the formation and composition of the vinyl-compound by a careful and frequently repeated analysis of the platinum-salt, which had been obtained from the products of four different operations. The salts of vinyl-triethyl-phosphonium resemble the oxethylated compounds. I have prepared the iodide, which crystallizes, but is extremely soluble, even in absolute alcohol.

The formation of the vinyl-compound was observed in several other processes, which may here be briefly mentioned, although I must state at once that the experimental evidence on which these observations are based is less conclusive.

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